{In Archive} Synthetic Turf Council Artificial turf presentation
Rick Doyle
to:
Jacqueline McQueen
05/30/2008 03:12 PM
Cc:
Ross Highsmith, Linda Sheldon, Kent Thomas, Michael Firestone, Walter Cybulski, Cathy Fehrenbacher, "'Tuncer B. Edil'", "Stanley H. Greene", marty.sergi, "Joseph E Motz"
Hide Details
From: "Rick Doyle" <rick@syntheticturfcouncil.org> Sort List...
To: Jacqueline McQueen/DC/USEPA/US@EPA,
Cc: Ross Highsmith/RTP/USEPA/US@EPA, Linda Sheldon/RTP/USEPA/US@EPA, Kent Thomas/RTP/USEPA/US@EPA, Michael Firestone/DC/USEPA/US@EPA, Walter Cybulski/DC/USEPA/US@EPA, Cathy Fehrenbacher/DC/USEPA/US@EPA, "'Tuncer B. Edil'" <tbedil@wisc.edu>, "Stanley H. Greene" <sgreene@sprinturf.com>, <marty.sergi@permalife.com>, "Joseph E Motz" <jmotz@themotzgroup.com>
History: This message has been replied to.
Archive: This message is being viewed in an archive.

5 Attachments

Broderick-Air Sampling for PAH's Comsewogue HS 10-07 .pdf

Broderick-Air Sampling for PAH's Schreiber HS 10-07 .pdf Tuncer Edil-Univ. of Wisc.-Madison.pdf

Health-Env. Impact of SBR Infill-Birkholz.pdf Twenty Questions.pdf

Dear Jackie and the EPA Workgroup on Crumb Rubber - The STC team is looking forward to meeting with you by conference call on Monday, June 2 at 10 a.m. Eastern to present information and expert knowledge relevant to your topic, "Assessing Human Exposures to Tire Crumb Contaminants Used In Playgrounds and Artificial Turf Fields." To access the conference call we will call [redacted]

The STC Team includes, in addition to me:

- Tuncer Edil, Ph.D., Professor and Research Director, Department of Civil and Environmental Engineering, University of Wisconsin-Madison (Bio attached)
- Stanley Greene, CEO, Sprinturf, builder of synthetic turf sports field
- Marty Sergi, CEO, Permalife Products, manufacturer of crumb rubber

I have created a PowerPoint presentation that you will be able to view from your PC, by logging onto h[redacted] just prior to the meeting and selecting Join a Meeting (I will send you an email invitation on Monday). During our presentation, Dr. Edil will reference Sections 6, 21, and 40 of a compendium of relevant research that has been published by one of our member companies, FieldTurf Tarkett. The volume is available to you on the following website: www.fieldturf.com/pdfs/sbr_TheStudies.pdf. In addition, we suggest you review at some point the excellent studies/technical documents found in Sections 5, 14, 41, and in the attachments to this email.

Please let me know if you have any questions. We look forward to an interactive and productive meeting. Best regards. Cheers, Rick

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---

Rick Doyle, President
Synthetic Turf Council
www.syntheticturfcouncil.org

400 Galleria Parkway |Suite 1500
Atlanta |GA | 30339
p 678.385.6720 | f 678.385.6501

-----Original Message-----
From: McQueen.Jacqueline@epamail.epa.gov [mailto:McQueen.Jacqueline@epamail.epa.gov]

Sent: Friday, May 30, 2008 8:55 AM
To: Rick Doyle
Cc: McQueen.Jacqueline@epamail.epa.gov; Highsmith.Ross@epamail.epa.gov; Sheldon.Linda@epamail.epa.gov; thomas.kent@epamail.epa.gov; Firestone.Michael@epamail.epa.gov; Cybulski.Walter@epamail.epa.gov; Fehrenbacher.Cathy@epamail.epa.gov
Subject: Artificial turf presentation: Sending e:mails to Rick Doyle for Monday meeting

Rick

I am sending this message so you have the e:mails for the Monday meeting attendees. Just respond to this if you want to send a link so we can access materials for Monday.

Thanks,

Jackie

Jacqueline McQueen
U.S. Environmental Protection Agency (8104R)
Office of Research and Development
Office of Science Policy
1200 Pennsylvania Avenue, N.W.
Washington, D.C. 20460
(202) 564-6639

{In Archive} Artificial turf presentation
Jacqueline McQueen to: Rick Doyle 05/19/2008 10:30 AM
Bcc: Ross Highsmith, Walter Cybulski

From: Jacqueline McQueen/DC/USEPA/US
To: "Rick Doyle" <rick@syntheticturfcouncil.org>,
Bcc: Ross Highsmith/RTP/USEPA/US@EPA, Walter Cybulski/DC/USEPA/US@EPA

Archive: This message is being viewed in an archive.

Hi, Rick! It was good to meet you last week. We are happy to set up a presentation for the Agency workgroup. Just to be clear, for the presentation, we'd focus on the science, not really the benefits (although you are welcome to summarize those as well). Here are some topics that I think would be useful to cover:

- Production info., including # of tires used/year, types of tires used, etc..
- How the turf is assembled (you all covered that in your talk last week), and where the recycled tires are used in the system (e.g., infill, but are they also in the underlying mat?).
- Standards for size for the individual infill particles.
- Chemical analysis of existing fields, and whether or not climate or region has any role in determining the chemical composition of the field.
- Summary of any existing analyses, whether or not you are planning on doing any of your own analyses, know of any ongoing studies, or would be interested in working with EPA on studies.
- Summary of any human exposure data.
- Any precautions the industry takes to exclude certain materials (e.g., metal strains, fibers) from the production process.
- Info. on any organizations that represent your industry and recycled rubber for other consumer applications. (We are trying to understand the similarities and differences of turf vs. tire crumb uses in mulch, playgrounds, etc.)

I realize that you might not have info. for all of these points. Our scientists are just beginning to try and understand your industry and related industries, how the materials are made, and ultimately, whether or not there is any potential chemical exposure to people, primarily children, from playing on the fields.

As mentioned last week, our group is looking mostly at tire crumbs/infill. This material is also used in mat and loose form under playground equipment, and I think as mulch chips; but we have no information at present on whether the materials used for artificial turf differ from the materials used for playgrounds and mulch.

We are looking at this from a scientific perspective only - we are not setting policy or contemplating regulations. So, this is really an information-gathering exercise to begin to characterize possible exposures.

Let's talk about possible dates and times for a presentation. The workgroup is scattered among various EPA offices, labs, centers, and regions, so a conference call will work well. Of course, you are welcome to come here if you'd like.

Anyway, let me know if you have questions, and possible dates for the presentation, and we will go from there.

Many thanks for your help.

Jackie

Jacqueline McQueen

"Rick Doyle"
<rick@synthetict
urfcouncil.org>

05/19/2008 07:45
AM

To: Jacqueline McQueen/DC/USEPA/US@EPA

cc

Subject

Jackie - I sent this last Friday and mistyped your email address.
Enjoyed meeting you.? Cheers, Rick

Rick Doyle, President
Synthetic Turf Council
www.syntheticturfcouncil.org

400 Galleria Parkway |Suite 1500
Atlanta |GA | 30339
p 678.385.6720 | f 678.385.6501

[attachment "STC Letter to Cleland-Hamnett-EPA 5-16-08.doc" deleted by Jacqueline McQueen/DC/USEPA/US]

J.C. Broderick & Associates, Inc.
Environmental Consulting & Testing

1201 Lake Avenue
Saint James, New York 11780
631.584.5492
Fax 631.584.2395
www.jcbroderick.com

October 30, 2007

Mr. Montgomery Granger
Comsewogue Union Free School District
Buildings & Grounds
290 Norwood Avenue
Port Jefferson Station, New York 11776-2598

Re: **Ambient Air Sampling for PAH's**
Comsewogue High School Football Field
565 Bicycle Path
Port Jeff Station, NY 11776
Sampling Date: October 16, 2007

JCB#: **07-12062**

Dear Mr. Granger:

J. C. Broderick & Associates, Inc. (JCB) was retained to perform air sampling at the above referenced athletic field due to concerns raised in the News 12 Long Island Focus 12 segment which aired on October 15, 2007 pertaining to artificial playing fields.

Specifically, News 12 reported that they collected samples of a "Port Washington field for lab studies" and reported the presence of three cancer-causing chemicals that were in excess of state safety levels. During the viewing of the News 12 segment, a New York State Department of Environmental Conservation (NYS DEC) logo was displayed suggesting that the turf sampling results were compared to NYS DEC published "safe levels". It should be noted that the NYS DEC does not establish "safe limits" for human exposure to chemicals and or hazardous substances, instead, they identify levels designed to protect the environment (e.g. soil clean up projects, water quality, etc.). Therefore it appears that News 12 may have erroneously compared their data to NYS DEC guidelines, which have been established to protect the environment and not as a means of determining the potential for human exposure or "safe limits." Since JCB does not have a copy of News 12's sampling methodology, laboratory analytical report, and or the state document referencing "safety levels", we can not comment on the accuracy and or reliability of their findings.

The News 12 Focus segment reported the following chemicals, classified as polycyclic aromatic hydrocarbons or PAHs, "in excess of state safety levels":

- Pyrene,
- BenzoPyrene, and
- Chrysene.

It is not disputed that the chemicals identified in News 12's sample are typically present within the matrix of the rubber used to make synthetic fields; therefore this study focuses on the potential routes of exposure for users (athletes, coaches, etc.) to be exposed to these chemicals while using the athletic field.

Background Information on Polycyclic Aromatic Hydrocarbons

The Agency for Toxic Substances and Disease Registry (ATSDR) states that PAHs are a group of over 100 different chemicals that are formed during the incomplete burning of coal, oil and gas, garbage, or other organic substances like tobacco or charbroiled meat. PAHs are usually found as a mixture containing two or more of these compounds, such as soot. Some PAHs are naturally occurring in the environment, while others are manufactured. PAHs are found in coal tar, crude oil, creosote, and roofing tar, asphalt and some are used in medicines or to make dyes, plastics, and pesticides.

Some types of PAH's have been identified as carcinogenic, or cancer causing, agents. The Occupational Safety and Health Administration (OSHA), the National Institute for Occupational Health and Safety (NIOSH) and the American Congress of Governmental Industrial Hygienists (ACGIH) have all promulgated occupational exposure limits to airborne concentrations of PAH's.

Dermal Absorption

PAHs can be absorbed through the skin (dermal exposure). Typical exposures come from the handing of contaminated soil or bathing in contaminated water. Absorption exposure of low levels can also occur in people who use PAH-containing medicated skin creams or shampoos.

In the case of synthetic athletic fields, like the one at the above referenced facility, PAH's are found within the matrix of the rubber, therefore, exposure to PAH's through skin contact with the surface of the athletic field during normal use is unlikely. More significant potential exposure routes include ingestion and inhalation.

Ingestion Hazard

PAH exposure can occur through ingestion. It has been reported that eating foods grown in contaminated soils and by eating grilled foods can increase the amount of PAHs in the food. Other foods that may contain low levels of PAHs include roasted coffee, roasted peanuts, refined vegetable oil, grains, vegetables and fruits. It has been reported that the general population ingests 1-9 micrograms of PAHs per day through consumption of food, making food the primary route of exposure.

It is anticipated that there will be some residue from the rubber material (e.g. rubber crumbs) of the athletic field at the above referenced facility, and when adhered to the children's hands or picked up could be ingested. However it is expected that the PAHs will leave the body through urine and feces in just a matter of days. The rubber matrix is not expected to be easily absorbed by the body during the digestive process and therefore would not be considered a significant threat. To minimize and or eliminate this potential exposure it is recommended that all users of the field be instructed to wash their hands and skin after playing on the field. In general, it is a good practice to always encourage and utilize good hygiene amongst athletes, regardless of whether the playing field is artificial or natural.

Inhalation

Most studies and literature on PAH exposure indicate that inhalation, or breathing of contaminated air, is a common route of exposure. Inhalation exposure can be attributed to breathing in fumes from vehicle exhaust, coal, coal tar, asphalt, wild fires, agricultural burning and cigarette/tobacco smoke. The operation of the athletic field does not typically include "burning it" and therefore this type of fume release is not an anticipated form of exposure.

PAHs are semi-volatile compounds, which mean that they do not easily evaporate. It is expected that the rubber material will have to be heated to a temperature of approximately 250 °F for any significant amount of the PAHs to evaporate from the rubber material. It is not expected that the field material will reach this temperature during ambient conditions and uses.

If the rubber field material did reach this temperature and PAHs did evaporate, they would be out-gassing to an outdoor, open field environment. Which means that the concentrations or presence of these parameters would be diluted immediately with the ambient air and would not reasonably be expected to be present at any harmful concentration.

Inhalation of airborne PAH's while utilizing the above referenced athletic field for its intended purposes, does not appear to be a feasible means of exposure and is unlikely. However as a quality assurance measure, PAH air sampling on and around the above referenced playing field was conducted.

Air Sampling Protocol

The air sampling was performed utilizing laboratory supplied sorbent tubes in accordance with the NIOSH Manual of Analytical Methods (NMAM) Method 5515, Polynuclear Aromatic Hydrocarbons by GC (fourth edition 8/15/94). The samples were collected by an experienced JCB environmental sampling technician, assigned individual identification numbers, logged into a chain of custody document, and delivered via courier to an independent environmental laboratory approval program

(ELAP) certified laboratory for analysis.

Air Sampling Results

The PAH air testing, performed on and around the athletic field of the above referenced facility, did not reveal the presence of any detectable concentrations of PAH's. All sixteen PAH's analyzed were found to be below the laboratory minimum detection limit (MDL) of 6 micrograms per cubic meter (ug/m^3). It should be noted that, the three types of PAH's identified in the News 12 investigation (Chrysene, Benzo(a)pyrene, and Pyrene), were observed below the laboratory MDL. A copy of the chain of custody form, laboratory analytical report, and laboratory analytical method can be referenced as an attachment to this letter.

Recommendations

Based upon the information reviewed on PAH exposure in humans and the results of the PAH air testing performed, the potential for exposure to PAH's during normal use of the athletic field, at the above referenced facility, appears to be minimal or insignificant.

However, to minimize any potential for exposure the following is recommended:

- Emphasize good hygiene practices (e.g. washing hands, showering, routine cleaning of uniforms, etc.) by athletes using the field,
- In the event that there is a school function during which younger children with the significant potential to put the synthetic turf, or pieces of rubber in their mouth exists, adult supervision should be present.

If you have any questions or are in need of additional information, please feel free to contact me.

Sincerely,

Brendan Broderick
J. C. Broderick & Associates, Inc.

Attch.

J.C. BRODERICK & ASSOCIATES

AIR MONITORING & CHAIN OF CUSTODY RECORD

(19)

PROJECT NAME/LOCATION	PROJECT #	DATE	LABORATORY		OST-ABATE	TURNAROUND TIME
Conservogue High School	07-12062	10/16/07	LIAL	☐ 0035174		
ADDRESS: 565 Bicycle Path Port Jeff Station, NY	WORK AREA: Exterior			☐	HR	☐ 12 HR
CLIENT: Conservogue UFSD	A=Air B=Bulk W=Wipe L=Liquid S=Soil			☐	4 HR	☐ OTHER____

SAMPLE ID	DATE	LAB #	TYPE		SAMPLE LOCATION/DESCRIPTION	FLOW B/E (L)	FLOW AVG (L)	BEGIN TIME	END TIME	TOTAL MIN	TOTAL VOL (L)	ANALYSIS METHOD	RESULT
SV1-A	10/16		A	☐ IWA ☐ OWA	North Parking Lot		1146937				200	8270 VAH only	
SV1-B	10/16		A	☐ IWA ☐ OWA	North Parking Lot		1146938				200	8270 VAH only	
SV2-A	10/16		A	☐ IWA ☐ OWA	Synthetic Turf Field		1146939				200	8270 VAH only	
SV2-B	10/16		A	☐ IWA ☐ OWA	Synthetic Turf Field		1146940				200	8270 VAH only	
FB-1	10/16		A	☐ IWA ☐ OWA	Field Blank		1146941						
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									

SAMPLERS NAME (PRINT)	SAMPLERS SIGNATURE	DATE	TIME	RECEIVED BY	SIGNATURE	DATE	TIME
Bryan Ezekius	[signature]	10/16/07	20:45		[signature]	10-18-07	9:15A
RELINQUISHED (PRINT)	SIGNATURE	DATE	TIME	ANALYST (PRINT)	SIGNATURE	DATE	TIME

COMMENTS:

☐ ANALYZE EACH MATERIAL TO 1st POSITIVE

☒ FAX RESULTS TO (631) 584-3395

☐ FAX RESULTS TO (631) 696-1158

MANAGER: Ed

J.C. Broderick & Associates • 420 Lake Avenue, St. James, NY 11780 • (Bill to Accounts Payable) • 631-584-5492 Phone, 631-584-3395 Fax

White-Laboratory Yellow-Office Pink-Field

LONG ISLAND ANALYTICAL LABORATORIES INC.

NY3DOH ELAP# 11693
USEPA# NY01273
CTDOH# PH-0284
AIHA# 164456
NJDEP# NY012
PADEP# 68-2943

"TOMORROWS ANALYTICAL SOLUTIONS TODAY"

October 19, 2007

J.C. Broderick & Associates
Brendan Broderick
420 Lake Avenue
Saint James, NY 11780

[illegible] High School

Dear Mr. Broderick:

Enclosed please find the Laboratory Analysis Report(s) for sample(s) received on October 18, 2007. Long Island Analytical Laboratories analyzed the samples on October 18, 2007 for the following:

CLIENT ID	ANALYSIS
SV-1A North Parking Lot	EPA 8270PAH
SV1-B North Parking Lot	EPA 8270PAH
SV2-A Synthetic Turf Field	EPA 8270PAH
SV2-B Synthetic Turf Field	EPA 8270PAH
FB-1 Field Blank	EPA 8270PAH

If you have any questions or require further information, please call at your convenience. Long Island Analytical Laboratories Inc. is a NELAP accredited laboratory. All reported results meet the requirements of the NELAP standards unless noted above. Report shall not be reproduced except in full, without the written approval of the laboratory. Long Island Analytical Laboratories would like to thank you for the opportunity to be of service to you.

Best Regards,

Long Island Analytical Laboratories, Inc.

110 Colin Drive · Holbrook, New York 11741
Phone (631) 472-3400 · Fax (631) 472-8505 · Email: LIAL@lialinc.com

Client: JC Broderick	Client ID: Comsewogue High School (SV-1A North Parking Lot)
Date received: 10/18/07	Laboratory ID: 1146937
Date extracted: 10/18/07	Matrix: Air
Date analyzed: 10/18/07	ELAP #: 11693

EPA METHOD 8270-PAH

PARAMETER	CAS No	MDL	RESULTS ug/m^3	Flag
ACENAPHTHENE	83-32-9	6 ug/m^3	<6	
ACENAPHTHYLENE	208-96-8	6 ug/m^3	<6	
ANTHRACENE	120-12-7	6 ug/m^3	<6	
BENZO(a)ANTHRACENE	56-55-3	6 ug/m^3	<6	
BENZO(a)PYRENE	50-32-8	6 ug/m^3	<6	
BENZO(b)FLUORANTHENE	205-99-2	6 ug/m^3	<6	
BENZO(ghi)PERYLENE	191-24-2	6 ug/m^3	<6	
BENZO(k)FLUORANTHENE	207-08-9	6 ug/m^3	<6	
CHRYSENE	218-01-9	6 ug/m^3	<6	
DIBENZO(a,h)ANTHRACENE	53-70-3	6 ug/m^3	<6	
FLUORANTHENE	206-44-0	6 ug/m^3	<6	
FLUORENE	86-73-7	6 ug/m^3	<6	
INDENO(1,2,3-cd)PYRENE	193-39-5	6 ug/m^3	<6	
NAPHTHALENE	91-20-3	6 ug/m^3	<6	
PHENANTHRENE	85-01-8	6 ug/m^3	<6	
PYRENE	129-00-0	6 ug/m^3	<6	

MDL = Minimum Detection Limit.

Calculated on a wet weight basis

Michael Veraldi

Michael Veraldi-Laboratory Director

110 Colin Drive • Holbrook, New York 11741
Phone (631) 472-3400 • Fax (631) 472-8505 • Email: LIAL@lialinc.com

Client: JC Broderick	Client ID: Comsewogue High School (SV-1B North Parking Lot)
Date received: 10/18/07	Laboratory ID: 1146938
Date extracted: 10/18/07	Matrix: Air
Date analyzed: 10/18/07	ELAP #: 11693

EPA METHOD 8270-PAH

PARAMETER	CAS No	MDL	RESULTS ug/m^3	Flag
ACENAPHTHENE	83-32-9	6 ug/m^3	<6	
ACENAPHTHYLENE	208-96-8	6 ug/m^3	<6	
ANTHRACENE	120-12-7	6 ug/m^3	<6	
BENZO(a)ANTHRACENE	56-55-3	6 ug/m^3	<6	
BENZO(a)PYRENE	50-32-8	6 ug/m^3	<6	
BENZO(b)FLUORANTHENE	205-99-2	6 ug/m^3	<6	
BENZO(ghi)PERYLENE	191-24-2	6 ug/m^3	<6	
BENZO(k)FLUORANTHENE	207-08-9	6 ug/m^3	<6	
CHRYSENE	218-01-9	6 ug/m^3	<6	
DIBENZO(a,h)ANTHRACENE	53-70-3	6 ug/m^3	<6	
FLUORANTHENE	206-44-0	6 ug/m^3	<6	
FLUORENE	86-73-7	6 ug/m^3	<6	
INDENO(1,2,3-cd)PYRENE	193-39-5	6 ug/m^3	<6	
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PYRENE	129-00-0	6 ug/m^3	<6	

MDL = Minimum Detection Limit.

Calculated on a wet weight basis

Michael Veraldi

Michael Veraldi-Laboratory Director

LONG ISLAND ANALYTICAL LABORATORIES INC.
"TOMORROWS ANALYTICAL SOLUTIONS TODAY"
110 Colin Drive · Holbrook, New York 11741
Phone (631) 472-3400 · Fax (631) 472-8505 · Email: LIAL@lialinc.com

Client: JC Broderick	Client ID: Comsewogue High School (SV2-A Synthetic Turf Field)
Date received: 10/18/07	Laboratory ID: 1146939
Date extracted: 10/18/07	Matrix: Air
Date analyzed: 10/18/07	ELAP #: 11693

EPA METHOD 8270-PAH

PARAMETER	CAS No	MDL	RESULTS ug/m^3	Flag
ACENAPHTHENE	83-32-9	6 ug/m^3	<6	
ACENAPHTHYLENE	208-96-8	6 ug/m^3	<6	
ANTHRACENE	120-12-7	6 ug/m^3	<6	
BENZO(a)ANTHRACENE	56-55-3	6 ug/m^3	<6	
BENZO(a)PYRENE	50-32-8	6 ug/m^3	<6	
BENZO(b)FLUORANTHENE	205-99-2	6 ug/m^3	<6	
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BENZO(k)FLUORANTHENE	207-08-9	6 ug/m^3	<6	
CHRYSENE	218-01-9	6 ug/m^3	<6	
DIBENZO(a,h)ANTHRACENE	53-70-3	6 ug/m^3	<6	
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FLUORENE	86-73-7	6 ug/m^3	<6	
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PHENANTHRENE	85-01-8	6 ug/m^3	<6	
PYRENE	129-00-0	6 ug/m^3	<6	

MDL = Minimum Detection Limit.

Calculated on a wet weight basis

Michael Veraldi

Michael Veraldi-Laboratory Director

Client: JC Broderick	Client ID: Comsewogue High School (SV2-B Synthetic Turf Field)
Date received: 10/18/07	Laboratory ID: 1146940
Date extracted: 10/18/07	Matrix: Air
Date analyzed: 10/18/07	ELAP #: 11693

EPA METHOD 8270-PAH

PARAMETER	CAS No	MDL	RESULTS ug/m^3	Flag
ACENAPHTHENE	83-32-9	6 ug/m^3	<6	
ACENAPHTHYLENE	208-96-8	6 ug/m^3	<6	
ANTHRACENE	120-12-7	6 ug/m^3	<6	
BENZO(a)ANTHRACENE	56-55-3	6 ug/m^3	<6	
BENZO(a)PYRENE	50-32-8	6 ug/m^3	<6	
BENZO(b)FLUORANTHENE	205-99-2	6 ug/m^3	<6	
BENZO(ghi)PERYLENE	191-24-2	6 ug/m^3	<6	
BENZO(k)FLUORANTHENE	207-08-9	6 ug/m^3	<6	
CHRYSENE	218-01-9	6 ug/m^3	<6	
DIBENZO(a,h)ANTHRACENE	53-70-3	6 ug/m^3	<6	
FLUORANTHENE	206-44-0	6 ug/m^3	<6	
FLUORENE	86-73-7	6 ug/m^3	<6	
INDENO(1,2,3-cd)PYRENE	193-39-5	6 ug/m^3	<6	
NAPHTHALENE	91-20-3	6 ug/m^3	<6	
PHENANTHRENE	85-01-8	6 ug/m^3	<6	
PYRENE	129-00-0	6 ug/m^3	<6	

MDL = Minimum Detection Limit. Calculated on a wet weight basis

Michael Veraldi

Michael Veraldi-Laboratory Director

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POLYNUCLEAR AROMATIC HYDROCARBONS by GC 5515

Table 1 MW: Table 1 CAS: Table 2 RTECS: Table 2

METHOD: 5515, Issue 2 EVALUATION: PARTIAL Issue 1: 15 May 1985
Issue 2: 15 August 1994

NIOSH: Table 3
OSHA :
PROPERTIES: Table 1

COMPOUNDS: acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, benzo[e]pyrene, chrysene, dibenz[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, pyrene

SYNONYMS: PAH; PNA; also see Table 2.

SAMPLING

SAMPLER: FILTER + SORBENT (2-µm, 37-mm PTFE + washed XAD-2, 100 mg/50 mg)

FLOW RATE: 2 L/min

VOL-MIN: 200 L
-MAX: 1000 L

SHIPMENT: transfer filters to culture tubes; wrap sorbent and culture tubes in Al foil; ship @ 0 °C

SAMPLE STABILITY: unknown; protect from heat and UV radiation

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 6 to 10

AREA SAMPLES: 8 replicates on preweighed filters for solvent selection

ACCURACY

RANGE STUDIED, ACCURACY, BIAS, and OVERALL PRECISION ($\hat{S}_{rT}$): not measured

MEASUREMENT

METHOD: GAS CHROMATOGRAPHY, CAPILLARY COLUMN, FID

ANALYTE: compounds above

EXTRACTION: 5 mL organic solvent appropriate to sample matrix (step 7)

INJECTION VOLUME: 4 µL; 10:1 split

COLUMN: 30 m x 0.32-mm ID, fused silica capillary, 1-µm DB-5

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 250 °C
-PROGRAM: 130 to 290 °C @ 4 °C/min

GASES-CARRIER: He @ 1 mL/min
-MAKEUP: He @ 20 mL/min

LOD: ca. 0.3 to 0.5 µg per sample [1]

CALIBRATION: external standards in toluene

RANGE, LOD, and PRECISION ($\hat{S}_r$): EVALUATION OF METHOD

APPLICABILITY: The working range for B[a]P is 3 to 150 µg/m^3 for a 400-L air sample. Specific sample sets may require modification in filter extraction solvent, choice of measurement method, and measurement conditions.

INTERFERENCES: Any compound which elutes at the same GC retention time may interfere. Heat, ozone, NO_2, or UV light may cause sample degradation.

OTHER METHODS: This revises P&CAM 183 [2]. The spectrophotometric methods, P&CAM 184 and 186 [2], have not been revised. Method 5506 (HPLC) uses the same sampling technique and is more sensitive.

REAGENTS:

1. Filter extraction solvent: acetonitrile, benzene,* cyclohexane, methylene chloride,* or other appropriate solvents, pesticide grade (step 7).
2. Toluene, pesticide grade.
3. Water, distilled, deionized.
4. PAH reference standards,* appropriate to the PAH-containing matrix sampled.
5. Calibration stock solution, 0.25 mg/mL.* Check purity of each PAH reference standard by GC/FID, HPLC/fluorescence and/or melting point. Purify, if necessary, by recrystallization. Weigh 25 mg of each PAH into a 100-mL volumetric flask; dilute to volume with toluene. Stable six months if refrigerated and protected from light.
6. Helium, prepurified.
7. Hydrogen, dry.
8. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter. PTFE-laminated membrane filter, 2-µm pore size, 37-mm diameter (Gelman Zefluor, Membrana, Pleasantown, CA, or equivalent), backed by a spacer (37-mm OD, 32-mm ID) cut from a cellulose support pad or SKC #225-23, in cassette filter holder.
      NOTE 1: If sampling is to be done in bright sunlight, use opaque or foil-wrapped cassettes to prevent sample degradation.
      NOTE 2: Take filters to be preweighed from the filter package and allow to equilibrate 24 h with laboratory atmosphere before taring.
   b. Sorbent tube, connected to filter with minimum length PVC tubing. Plastic caps are required after sampling. Washed XAD-2 resin (front = 100 mg; back = 50 mg) (Supelco ORBO 43 or equivalent). Pressure drop at 2 L/min airflow 1.6 to 2 kPa (15 to 20 cm H_2O).
2. Personal sampling pump capable of operating for 8 h at 2 L/min, with flexible connecting tubing.
3. Aluminum foil.
4. Vial, scintillation, 20-mL, glass, PTFE-lined cap.
5. Refrigerant, bagged.
6. Culture tubes, PTFE-lined screw cap, 13-mm x 100-mm.
7. Forceps.
8. Filters, 0.45-µm, PTFE (for filtering sample solutions).
9. Pipet, 5-mL.
10. Syringes or micropipets, 1- to 100-µL.
11. Ultrasonic bath.
12. Gas chromatograph with FID, electronic integrator, and capillary column (page 5515-1).
13. Volumetric flasks, 10- and 100-mL.
14. Lighting in laboratory: incandescent or UV-shielded fluorescent.

SPECIAL PRECAUTIONS: Treat benzene, methylene chloride, and all polynuclear aromatic hydrocarbons as carcinogens. Neat compounds should be weighed in a glove box. Spent samples and unused standards are toxic waste. Regularly check counter tops and equipment with "black light" for fluorescence as an indicator of contamination by PAH.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Take personal samples at 2 L/min for a total sample size of 200 to 1000 L. Take a concurrent set of eight replicate area samples at 2 to 4 L/min on preweighed, 2-µm PTFE filters in an area of highest expected PAH concentration.
   NOTE: The area samples are needed for solvent selection (step 7).
3. Immediately after sampling, transfer the filter carefully with forceps to a scintillation vial. Hold filter at edge to avoid disturbing the deposit. Cap the scintillation vial and wrap it in aluminum foil.
   NOTE: This step is necessary to avoid loss of analytes due to sublimation and degradation by light.
4. Cap the sorbent tube and wrap it in aluminum foil.
5. Ship to laboratory in insulated container with bagged refrigerant.

SAMPLE PREPARATION:

NOTE: UV light may degrade PAH. Use yellow, UV-absorbing shields for fluorescent lights or use incandescent lighting.

6. Refrigerate samples upon receipt at laboratory.
7. Determine optimum extraction solvent.
   a. Allow the preweighed area filter samples to equilibrate 24 h with the laboratory atmosphere.
   b. Weigh the area filters. Determine total weight collected on each.
   c. Extract the first pair of area filters with acetronitrile, the second with benzene, the third with cyclohexane, and the fourth with methylene chloride, according to step 8.
      NOTE: Use alternate solvents, if appropriate. PAH of interest may be entrained within, and adsorbed by, particulate matter collected on the filter. It is necessary to determine the solvent which maximizes recovery of the PAH from each sample matrix. For example, methylene chloride [3,4] and benzene:ethanol (4:1 v/v) [5] have been recommended for extraction of PAH from diesel exhaust particulate.
   d. Analyze the extracts for the PAH of interest (steps 10 through 18). Normalize the total mass of PAH found to the mass of sample collected.
   e. Choose the solvent which gives the highest recovery of PAH of interest. Use the solvent chosen to extract the personal filter samples.
8. Extract filters.
   a. Add 5.0 mL of the solvent chosen in step 7 to each scintillation vial containing a filter. Start media and reagent blanks at this step.
   b. Cap and let stand 15 to 20 min in an ultrasonic bath.
      NOTE: Soxhlet extraction may be required when large amounts of highly adsorptive particulate matter (e.g., fly ash or diesel soot) are present.
9. Desorb PAH from sorbent.
   a. Score each sorbent tube with a file in front of the primary (larger) sorbent section. Break tube at score line.
   b. Transfer front glass wool plug and front sorbent section to a culture tube. Transfer back

sorbent section and the middle glass wool plug to a second culture tube.

c. Add 5.0 mL toluene to each culture tube. Cap the culture tubes.

d. Allow samples to stand for 30 min. Swirl occasionally.

10. Filter all sample extracts through an 0.45-µm membrane filter.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards.
    a. Dilute aliquots of calibration stock solution with toluene in 10-mL volumetric flasks (e.g., to 5, 1, 0.2, 0.05, and 0.005 µg/mL).
    b. Intersperse working standards and samples in the measurements.
    c. Prepare calibration graphs (peak area vs. µg of each PAH per sample).
12. Recovery and desorption efficiency.
    a. Determine recovery (R) from filters and desorption efficiency (DE) from sorbent tubes at least once for each lot of filters and sorbent tubes used in the range of interest.
        (1) Filters. Using a microliter syringe or micropipette, spike four filters at each of five concentration levels with calibration stock solution. Allow the filters to dry in the dark overnight. Analyze the filters (steps 8, 10, and 14 through 16). Prepare graphs of R vs. amounts found.

        NOTE: This step may not be used for some highly adsorptive particulate matrices for which calibration by the method of standard additions may be more accurate.

        (2) Sorbent tubes. Transfer an unused front sorbent section to a culture tube. prepare a total of 24 culture tubes in order to measure DE at five concentration levels plus blanks in quadruplicate. Using a microliter syringe or micropipette, add calibration stock solution directly to sorbent. Cap culture tubes and allow to stand overnight in the dark. Analyze (steps 9, 10, and 14 through 16). Prepare graphs of DE vs. amounts found.
    b. Check R and DE at two levels for each sample set, in duplicate. Repeat determination of R and DE graphs if checks do not agree to within ±5% of DE graph.
13. Analyze at least three field blanks for each sample medium.

MEASUREMENT:

14. Set GC according to manufacturer's recommendations and to the conditions on page 5515-1.
15. Inject sample aliquot. Start temperature program.
16. Measure peak areas.

    NOTE 1: Approximate retention times appear in Table 4.

    NOTE 2: If peak area is above the calibration range, dilute with appropriate solvent, reanalyze, and apply dilution factor in calculations.

    NOTE 3: If sample has many interferences, additional sample cleanup may be necessary. Many cleanup procedures have been published. Liquid-liquid partitioning between cyclohexane and nitromethane [6,7] is widely used, but other techniques may be more appropriate for specific samples.

CALCULATIONS:

17. Read the mass, µg (corrected for R or DE) of each analyte found on the filter (W) and front sorbent (W_f) and back sorbent (W_b) sections, and on the average media blank filter (B) and front sorbent (B_f) and back sorbent (B_b) sections from the calibration graphs.
18. Calculate concentration, C (mg/m^3), in air as the sum of the particulate concentration and the vapor concentration using the actual air volume sampled, V (L).

$$C = \frac{(W - B + W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Owing to large interferences that occured while utilizing NIOSH Method P&CAM 206 for samples collected during asphalt roofing operations, the gas chromatographic capillary column method was developed. The GC method has been evaluated using several hundred field filter and sorbent tube sampling trains. To date, no statistical studies have been initiated. Overall, standard spiked filters and sorbent tubes have yielded reproducible measurement calibration graphs. The method has been applied to the following sources with semi-quantitative results using three separate particulate extraction solvents (benzene, cyclohexane, acetonitrile): aluminum reduction facilities, asphalt fume, coal gasification plants, coal liquefaction plants, coal tar pitch, coke oven emissions, creosote treatment facilities, diesel exhaust, graphite electrode manufacturing, petroleum pitch, and roofing tearoff operations.

REFERENCES:

[1] UBTL, Inc., NIOSH Sequence #4220-O (NIOSH, unpublished, August 10, 1984).

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 1, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[3] Breuer, G. M. Anal. Lett., 17 (A11), 1293-1306 (1984).

[4] Zweidinger, R. B., S. B. Tejada, D. Dropkins, J. Huisingh, and L. Claxton. "Characterization of Extractable Organics in Diesel Exhaust Particulate," paper presented at Symposium on Diesel Particulate Emissions Measurement Characterization, Ann Arbor, MI (1978).

[5] Swarin, S. J. and R. L. Williams. "Liquid Chromatographic Determination of Benzo[a]pyrene in Diesel Exhaust Particulate: Verification of the Collection and Analytical Methods," Polynuclear Aromatic Hydrocarbons: Physical and Biological Effects, Bjorseth, A. and Dennis, Eds., Battelle Press, pp. 771-790 (1980).

[6] Wise, S. A., et al. "Analytical Methods for the Determination of Polycyclic Aromatic Hydrocarbons on Air Particulate Matter," Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry, Cooke, Dennis and Fisher, Eds., Battelle Press, pp. 919-929 (1982).

[7] Novotny, M., M. L. Lee and K. D. Bartle. J. Chromatog. Sci., 12, 606-612 (1974).

[8] Backup Data Report for Method 5506, Analytical Report for NIOSH Sequence 4170 (NIOSH, DPSE, MRSB, unpublished, March 16, 1984).

[9] Studt., P., Liebigs Ann. Chem., 528 (1978).

[10] Clar, E. Polycyclic Hydrocarbons, Academic Press (1964).

[11] Handbook of Chemistry and Physics, 62nd ed., CRC Press (1982).

[12] Beilstein 5 (1), 344.

METHOD REVISED BY:

B.R. Belinky, NIOSH/DPSE, and E.J. Slick; J.C. Holt, D.E. Bilak, and J.B. Perkins, DataChem Laboratories, Inc., Salt Lake City, UT.

Table 1. Formulae and physical properties.

COMPOUND (by M.W.)	EMPIRICAL FORMULA	MOLECULAR WEIGHT	MELTING POINT (°C)*	BOILING POINT (°C)*	REF.
1. NAPHTHALENE	$C_{10}H_8$	128.17	80.2	218	[10]
2. ACENAPHTHYLENE	$C_{12}H_8$	152.20	92-93	265-275	[11]
3. ACENAPHTHENE	$C_{12}H_{10}$	154.21	96.2	279	[11]
4. FLUORENE	$C_{13}H_{10}$	166.22	116	293-295	[10]
5. ANTHRACENE	$C_{14}H_{10}$	178.23	218	340	[10]
6. PHENANTHRENE	$C_{14}H_{10}$	178.23	100	340	[10]
7. FLUORANTHENE	$C_{16}H_{10}$	202.26	110	384*	[10], [12]
8. PYRENE	$C_{16}H_{10}$	202.26	156	393	[10]
9. BENZ[a]ANTHRACENE	$C_{18}H_{12}$	228.29	162-167	435	[10]
10. CHRYSENE	$C_{18}H_{12}$	228.29	255-256	448	[10]
11. BENZO[b]FLUORANTHENE	$C_{20}H_{12}$	252.32	168	--	[10]
12. BENZO[k]FLUORANTHENE	$C_{20}H_{12}$	252.32	217	480	[11]
13. BENZO[a]PYRENE	$C_{20}H_{12}$	252.32	179	495	[10]
14. BENZO[e]PYRENE	$C_{20}H_{12}$	252.32	178-179	--	[10]
15. BENZO[ghi]PERYLENE	$C_{22}H_{12}$	276.34	273	--	[10]
16. INDENO[1,2,3-cd]PYRENE	$C_{22}H_{12}$	276.34	161.5-163	530	[9]
17. DIBENZ[a,h]ANTHRACENE	$C_{22}H_{14}$	278.35	267	524	[10]

*Many of these compounds will sublime.

Table 2. Synonyms.

COMPOUND (alphabetically)	SYNONYMS
1. ACENAPHTHENE	CAS# 83-32-9; RTECS# AB1000000
2. ACENAPHTHYLENE	CAS# 208-96-8; RTECS# AB1254000
3. ANTHRACENE	CAS# 120-12-7; RTECS# CA9350000
4. BENZ[a]ANTHRACENE	1,2-benzanthracene; benzo[b]phenanthrene; 2,3-benzophenanthrene; tetraphene; CAS# 56-55-3; RTECS# CV9275000
5. BENZO[b]FLUORANTHENE	3,4-benzofluoranthene; 2,3-benzofluoranthene; benz[e]acephenanthrylene; B[b]F; CAS # 205-99-2; RTECS# CU1400000
6. BENZO[k]FLUORANTHENE	11,12-benzofluoranthene; CAS# 207-08-9; RTECS# DF6350000
7. BENZO[ghi]PERYLENE	1,12-benzoperylene; CAS# 191-24-2; RTECS# DI6200500
8. BENZO[a]PYRENE	3,4-benzopyrene; 6,7-benzopyrene; B[a]P; BP; CAS# 50-32-8; RTECS# DJ3675000
9. BENZO[e]PYRENE	1,2-benzopyrene; 4,5-benzopyrene; B[e]P; CAS# 192-97-2; RTECS# DJ4200000
10. CHRYSENE	1,2-benzophenanthrene; benzo[a]phenanthrene; CAS# 218-01-9; RTECS# GC0700000
11. DIBENZ[a,h]ANTHRACENE	1,2,5,6-dibenzanthracene; CAS# 53-70-3; RTECS# HN2625000
12. FLUORANTHENE	benzo[jk]fluorene; Idryl; CAS# 206-44-0; RTECS# LL4025000
13. FLUORENE	o-biphenylenemethane; CAS# 86-73-7; RTECS# LL5670000
14. INDENO[1,2,3-cd]PYRENE	2,3-phenylenepyrene; CAS# 193-39-5; RTECS# NK9300000
15. NAPHTHALENE	naphthene; CAS# 91-20-3; RTECS# QJ0525000
16. PHENANTHRENE	CAS# 85-01-8; RTECS# SF7175000
17. PYRENE	benzo[def]phenanthrene; CAS# 129-00-0; RTECS# UR2450000

Table 3. Exposure Limits.

COMPOUND (alphabetically)	OSHA	NIOSH	ACGIH
1. ACENAPHTHENE	--	--	--
2. ACENAPHTHYLENE	--	--	--
3. ANTHRACENE	0.2 mg/m^3	--	--
4. BENZ[A]ANTHRACENE	--	--	--
5. BENZO[B]FLUORANTHENE	--	--	suspect carcinogen
6. BENZO[K]FLUORANTHENE	--	--	--
7. BENZO[GHI]PERYLENE	--	--	--
8. BENZO[A]PYRENE	0.2 mg/m^3 (benzene sol.)	0.1 mg/m^3 (cyclohexane sol.)	suspect carcinogen
9. BENZO[E]PYRENE	--	--	--
10. CHRYSENE	0.2 mg/m^3 (benzene sol.)	lowest feasible, carcinogen	suspect carcinogen
11. DIBENZ[A,H]ANTHRACENE	--	--	--
12. FLUORANTHENE	--	--	--
13. FLUORENE	--	--	--
14. INDENO[1,2,3-CD]PYRENE	--	--	--
15. NAPHTHALENE	10 ppm	10 ppm; STEL 15 ppm	10 ppm; STEL 15 ppm
16. PHENANTHRENE	0.2 mg/m^3	--	--
17. PYRENE	--	--	--

Table 4. Approximate PAH retention times.

COMPOUND	RETENTION TIME (min)*
1. NAPHTHALENE	not available
2. ACENAPHTHALENE	7.66
3. ACENAPHTHENE	8.37
4. FLUORENE	10.5
5. PHENANTHRENE	15.0
6. ANTHRACENE	15.3
7. FLUORANTHENE	21.4
8. PYRENE	22.6
9. BENZ[a]ANTHRACENE	29.4
10. CHRYSENE	29.6
11. BENZO[e]PYRENE	36.4
12. BENZO[b]FLUORANTHENE	35.1
13. BENZO[k]FLUORANTHENE	35.2
14. BENZO[a]PYRENE	36.2
15. DIBENZ[a,h]ANTHRACENE	43.9
16. BENZO[ghi]PERYLENE	45.6
17. INDENO[1,2,3-cd]PYRENE	43.6

*NOTE: Actual retention times will vary with individual columns and column age.

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October 29, 2007

Mr. Eric Vonderhorst
Port Washington Union Free School District
Administration Building
90 Avenue C
Port Washington, New York 11050

Re: **Ambient Air Sampling for PAH's**
Schreiber High School Football Field
101 Campus Drive
Port Washington, New York 11050
Sampling Date: October 17, 2007

JCB#: **07-12078**

Dear Mr. Vonderhorst:

J. C. Broderick & Associates, Inc. (JCB) was retained to investigate the concerns raised in a News 12 Long Island "Focus 12: Toxic Turf" segment which aired on October 15, 2007. Specifically, News 12 reported that they collected samples of a "Port Washington field for lab studies" and reported the presence of three cancer-causing chemicals that were in excess of state safety levels.

During the viewing of the News 12 segment, a New York State Department of Environmental Conservation (NYS DEC) logo was displayed suggesting that the turf sampling results were compared to NYS DEC published "safe levels". It should be noted that the NYS DEC does not establish "safe limits" for human exposure to chemicals and or hazardous substances, instead, they identify levels designed to protect the environment (e.g. soil clean up projects, water quality, etc.). Therefore it appears that News 12 may have erroneously compared their data to NYS DEC guidelines, which have been established to protect the environment and not as a means of determining the potential for human exposure or "safe limits." Since JCB does not have a copy of News 12's sampling methodology, laboratory analytical report, and or the state document referencing "safety levels", we can not comment on the accuracy and or reliability of their findings.

The News 12 Focus segment reported the following chemicals, classified as polycyclic aromatic hydrocarbons or PAHs, "in excess of state safety levels":

- Pyrene,
- BenzoPyrene, and
- Chrysene.

It is not disputed that the chemicals identified in News 12's sample are typically present within the matrix of the rubber used to make synthetic fields; therefore this study focuses on the potential routes of exposure for users (athletes, coaches, etc.) to be exposed to these chemicals while using the athletic field.

Background Information on Polycyclic Aromatic Hydrocarbons

The Agency for Toxic Substances and Disease Registry (ATSDR) states that PAHs are a group of over 100 different chemicals that are formed during the incomplete burning of coal, oil and gas, garbage, or other organic substances like tobacco or charbroiled meat. PAHs are usually found as a mixture containing two or more of these compounds, such as soot. Some PAHs are naturally occurring in the environment, while others are manufactured. PAHs are found in coal tar, crude oil, creosote, and roofing tar, asphalt and some are used in medicines or to make dyes, plastics, and pesticides.

Some types of PAH's have been identified as carcinogenic, or cancer causing, agents. The Occupational Safety and Health Administration (OSHA), the National Institute for Occupational Health and Safety (NIOSH) and the American Congress of Governmental Industrial Hygienists (ACGIH) have all promulgated occupational exposure limits to airborne concentrations of PAH's.

Dermal Absorption

PAHs can be absorbed through the skin (dermal exposure). Typical exposures come from the handing of contaminated soil or bathing in contaminated water. Absorption exposure of low levels can also occur in people who use PAH-containing medicated skin creams or shampoos.

In the case of synthetic athletic fields, like the one at the above referenced facility, PAH's are found within the matrix of the rubber, therefore, exposure to PAH's through skin contact with the surface of the athletic field during normal use is unlikely. More significant potential exposure routes include ingestion and inhalation.

Ingestion Hazard

PAH exposure can occur through ingestion. It has been reported that eating foods grown in contaminated soils and by eating grilled foods can increase the amount of PAHs in the food. Other foods that may contain low levels of PAHs include roasted coffee, roasted peanuts, refined vegetable oil, grains, vegetables and fruits. It has been reported that the general population ingests 1-9 micrograms of PAHs per day through consumption of food, making food the primary route of exposure.

It is anticipated that there will be some residue from the rubber material (e.g. rubber crumbs) of the athletic field at the above referenced facility, and when adhered to the children's hands or picked up could be ingested. However it is expected that the PAHs will leave the body through urine and feces in just a matter of days. The rubber matrix is not expected to be easily absorbed by the body during the digestive process and therefore would not be considered a significant threat. To minimize and or eliminate this potential exposure it is recommended that all users of the field be instructed to wash their hands and skin after playing on the field. In general, it is a good practice to always encourage and utilize good hygiene amongst athletes, regardless of whether the playing field is artificial or natural.

Inhalation

Most studies and literature on PAH exposure indicate that inhalation, or breathing of contaminated air, is a common route of exposure. Inhalation exposure can be attributed to breathing in fumes from vehicle exhaust, coal, coal tar, asphalt, wild fires, agricultural burning and cigarette/tobacco smoke. The operation of the athletic field does not typically include "burning it" and therefore this type of fume release is not an anticipated form of exposure.

PAHs are semi-volatile compounds, which mean that they do not easily evaporate. It is expected that the rubber material will have to be heated to a temperature of approximately 250 °F for any significant amount of the PAHs to evaporate from the rubber material. It is not expected that the field material will reach this temperature during ambient conditions and uses.

If the rubber field material did reach this temperature and PAHs did evaporate, they would be out-gassing to an outdoor, open field environment. Which means that the concentrations or presence of these parameters would be diluted immediately with the ambient air and would not reasonably be expected to be present at any harmful concentration.

Inhalation of airborne PAH's while utilizing the above referenced athletic field for its intended purposes, does not appear to be a feasible means of exposure and is unlikely. However as a quality assurance measure, PAH air sampling on and around the above referenced playing field was conducted.

Air Sampling Protocol

The air sampling was performed utilizing laboratory supplied sorbent tubes in accordance with the NIOSH Manual of Analytical Methods (NMAM) Method 5515, Polynuclear Aromatic Hydrocarbons by GC (fourth edition 8/15/94). The samples were collected by an experienced JCB environmental sampling technician, assigned individual identification numbers, logged into a chain of custody document, and delivered via courier to an independent environmental laboratory approval program

(ELAP) certified laboratory for analysis.

<u>Air Sampling Results</u>

The PAH air testing, performed on and around the athletic field of the above referenced facility, did not reveal the presence of any detectable concentrations of PAH's. All sixteen PAH's analyzed were found to be below the laboratory minimum detection limit (MDL) of 6 micrograms per cubic meter (ug/m^3). It should be noted that, the three types of PAH's identified in the News 12 investigation (Chrysene, Benzo(a)pyrene, and Pyrene), were observed below the laboratory MDL. A copy of the chain of custody form, laboratory analytical report, and laboratory analytical method can be referenced as an attachment to this letter.

<u>Recommendations</u>

Based upon the information reviewed on PAH exposure in humans and the results of the PAH air testing performed, the potential for exposure to PAH's during normal use of the athletic field, at the above referenced facility, appears to be minimal or insignificant.

However, to minimize any potential for exposure the following is recommended:

- Emphasize good hygiene practices (e.g. washing hands, showering, routine cleaning of uniforms, etc.) by athletes using the field,

- In the event that there is a school function during which younger children with the significant potential to put the synthetic turf, or pieces of rubber in their mouth exists, adult supervision should be present.

If you have any questions or are in need of additional information, please feel free to contact me.

Sincerely,

Brendan Broderick
J. C. Broderick & Associates, Inc.

Attch.

J.C. BRODERICK & ASSOCIATES

AIR MONITORING & CHAIN OF CUSTODY RECORD (19)

0035172

0035172

PROJECT NAME/LOCATION: Schrieber High School
PROJECT #: 07-12078
DATE: 10/17/07
LABORATORY: LIAL
ADDRESS: Campus Dr. Port Washington, NY
WORK AREA: Exterior
CLIENT: Port Washington UFSD

A=Air B=Bulk W=Wipe L=Liquid S=Soil

POST-ABATE | TURNAROUND TIME
6 HR | ☐ 12 HR
24 HR | ☐ OTHER____

SAMPLE ID	DATE	LAB#	TYPE		SAMPLE LOCATION/DESCRIPTION	FLOW B/E (L)	FLOW AVG (L)	BEGIN TIME	END TIME	TOTAL MIN	TOTAL VOL (L)	ANALYSIS METHOD	RESULT
SV01-A	10/17		A	☐ IWA ☐ OWA	South East Corner of Building, NW corner of Field Hockey Field			114692	6		200	8270 PAH only	
SV2-A	10/17		A	☐ IWA ☐ OWA	Synthetic Turf Field			114692	7		200	8270 PAH only	
SV2-B	10/17		A	☐ IWA ☐ OWA	Synthetic Turf Field			114692	8		200	8270 PAH only	
FB-1	10/17		A	☐ IWA ☐ OWA	Field Blank			114692	9				
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									
				☐ IWA ☐ OWA									

SAMPLERS NAME (PRINT)	SAMPLERS SIGNATURE	DATE	TIME	RECEIVED BY	SIGNATURE	DATE	TIME
Bryan Ezelius	[signature]	10/17/07	15:00		[signature]	10-18-07	
RELINQUISHED (PRINT)	SIGNATURE	DATE	TIME	ANALYST (PRINT)	SIGNATURE	DATE	TIME

COMMENTS:

☐ ANALYZE EACH MATERIAL TO 1st POSITIVE
☒ FAX RESULTS TO (631) 584-3395
☐ FAX RESULTS TO (631) 696-1158

MANAGER: Ed

LONG ISLAND ANALYTICAL LABORATORIES INC.

NYSDOH ELAP# 11693
USEPA# NY01273
CTDOH# PH-0284
AIHA# 164456
NJDEP# NY012
PADEP# 68-2943

"TOMORROWS ANALYTICAL SOLUTIONS TODAY"

October 19, 2007

J.C. Broderick & Associates
Brendan Broderick
420 Lake Avenue
Saint James, NY 11780

[redacted]

Dear Mr. Broderick:

Enclosed please find the Laboratory Analysis Report(s) for sample(s) received on October 18, 2007. Long Island Analytical Laboratories analyzed the samples on October 18, 2007 for the following:

CLIENT ID	ANALYSIS
SV1-A SE Corner of Building	EPA 8270PAH
SV2-A Synthetic Turf Field	EPA 8270PAH
SV2-B Synthetic Turf Field	EPA 8270PAH
FB-1 Field Blank	EPA 8270PAH

If you have any questions or require further information, please call at your convenience. Long Island Analytical Laboratories Inc. is a NELAP accredited laboratory. All reported results meet the requirements of the NELAP standards unless noted above. Report shall not be reproduced except in full, without the written approval of the laboratory. Long Island Analytical Laboratories would like to thank you for the opportunity to be of service to you.

Best Regards,

Long Island Analytical Laboratories, Inc.

Client: JC Broderick	Client ID: Schrieber HS, Port Washington (FB-1)
Date received: 10/18/07	Laboratory ID: 1146929
Date extracted: 10/18/07	Matrix: Air
Date analyzed: 10/18/07	ELAP #: 11693

EPA METHOD 8270-PAH

PARAMETER	CAS No	MDL	RESULTS ug	Flag
ACENAPHTHENE	83-32-9	1 ug	<1	
ACENAPHTHYLENE	208-96-8	1 ug	<1	
ANTHRACENE	120-12-7	1 ug	<1	
BENZO(a)ANTHRACENE	56-55-3	1 ug	<1	
BENZO(a)PYRENE	50-32-8	1 ug	<1	
BENZO(b)FLUORANTHENE	205-99-2	1 ug	<1	
BENZO(ghi)PERYLENE	191-24-2	1 ug	<1	
BENZO(k)FLUORANTHENE	207-08-9	1 ug	<1	
CHRYSENE	218-01-9	1 ug	<1	
DIBENZO(a,h)ANTHRACENE	53-70-3	1 ug	<1	
FLUORANTHENE	206-44-0	1 ug	<1	
FLUORENE	86-73-7	1 ug	<1	
INDENO(1,2,3-cd)PYRENE	193-39-5	1 ug	<1	
NAPHTHALENE	91-20-3	1 ug	<1	
PHENANTHRENE	85-01-8	1 ug	<1	
PYRENE	129-00-0	1 ug	<1	

MDL = Minimum Detection Limit.

Calculated on a wet weight basis

Michael Veraldi

Michael Veraldi-Laboratory Director

LONG ISLAND ANALYTICAL LABORATORES INC.
"TOMORROWS ANALYTICAL SOLUTIONS TODAY"
110 Colin Drive · Holbrook, New York 11741
Phone (631) 472-3400 · Fax (631) 472-8505 · Email: LIAL@lialinc.com

Client: JC Broderick	Client ID: Schrieber HS, Port Washington (SV1-A Corner of Building)
Date received: 10/18/07	Laboratory ID: 1146926
Date extracted: 10/18/07	Matrix: Air
Date analyzed: 10/18/07	ELAP #: 11693

EPA METHOD 8270-PAH

PARAMETER	CAS No	MDL	RESULTS ug/m³	Flag
ACENAPHTHENE	83-32-9	6 ug/m³	<6	
ACENAPHTHYLENE	208-96-8	6 ug/m³	<6	
ANTHRACENE	120-12-7	6 ug/m³	<6	
BENZO(a)ANTHRACENE	56-55-3	6 ug/m³	<6	
BENZO(a)PYRENE	50-32-8	6 ug/m³	<6	
BENZO(b)FLUORANTHENE	205-99-2	6 ug/m³	<6	
BENZO(ghi)PERYLENE	191-24-2	6 ug/m³	<6	
BENZO(k)FLUORANTHENE	207-08-9	6 ug/m³	<6	
CHRYSENE	218-01-9	6 ug/m³	<6	
DIBENZO(a,h)ANTHRACENE	53-70-3	6 ug/m³	<6	
FLUORANTHENE	206-44-0	6 ug/m³	<6	
FLUORENE	86-73-7	6 ug/m³	<6	
INDENO(1,2,3-cd)PYRENE	193-39-5	6 ug/m³	<6	
NAPHTHALENE	91-20-3	6 ug/m³	<6	
PHENANTHRENE	85-01-8	6 ug/m³	<6	
PYRENE	129-00-0	6 ug/m³	<6	

MDL = Minimum Detection Limit.

Calculated on a wet weight basis

Michael Veraldi

Michael Veraldi-Laboratory Director

Client: JC Broderick	Client ID: Schrieber HS, Port Washington (SV2-A Synthetic Turf Field)
Date received: 10/18/07	Laboratory ID: 1146927
Date extracted: 10/18/07	Matrix: Air
Date analyzed: 10/18/07	ELAP #: 11693

EPA METHOD 8270-PAH

PARAMETER	CAS No	MDL	RESULTS ug/m^3	Flag
ACENAPHTHENE	83-32-9	6 ug/m^3	<6	
ACENAPHTHYLENE	208-96-8	6 ug/m^3	<6	
ANTHRACENE	120-12-7	6 ug/m^3	<6	
BENZO(a)ANTHRACENE	56-55-3	6 ug/m^3	<6	
BENZO(a)PYRENE	50-32-8	6 ug/m^3	<6	
BENZO(b)FLUORANTHENE	205-99-2	6 ug/m^3	<6	
BENZO(ghi)PERYLENE	191-24-2	6 ug/m^3	<6	
BENZO(k)FLUORANTHENE	207-08-9	6 ug/m^3	<6	
CHRYSENE	218-01-9	6 ug/m^3	<6	
DIBENZO(a,h)ANTHRACENE	53-70-3	6 ug/m^3	<6	
FLUORANTHENE	206-44-0	6 ug/m^3	<6	
FLUORENE	86-73-7	6 ug/m^3	<6	
INDENO(1,2,3-cd)PYRENE	193-39-5	6 ug/m^3	<6	
NAPHTHALENE	91-20-3	6 ug/m^3	<6	
PHENANTHRENE	85-01-8	6 ug/m^3	<6	
PYRENE	129-00-0	6 ug/m^3	<6	

MDL = Minimum Detection Limit.

Calculated on a wet weight basis

Michael Veraldi

Michael Veraldi-Laboratory Director

Client: JC Broderick	Client ID: Schrieber HS, Port Washington (SV2-B Synthetic Turf Field)
Date received: 10/18/07	Laboratory ID: 1146928
Date extracted: 10/18/07	Matrix: Air
Date analyzed: 10/18/07	ELAP #: 11693

EPA METHOD 8270-PAH

PARAMETER	CAS No	MDL	RESULTS ug/m^3	Flag
ACENAPHTHENE	83-32-9	6 ug/m^3	<6	
ACENAPHTHYLENE	208-96-8	6 ug/m^3	<6	
ANTHRACENE	120-12-7	6 ug/m^3	<6	
BENZO(a)ANTHRACENE	56-55-3	6 ug/m^3	<6	
BENZO(a)PYRENE	50-32-8	6 ug/m^3	<6	
BENZO(b)FLUORANTHENE	205-99-2	6 ug/m^3	<6	
BENZO(ghi)PERYLENE	191-24-2	6 ug/m^3	<6	
BENZO(k)FLUORANTHENE	207-08-9	6 ug/m^3	<6	
CHRYSENE	218-01-9	6 ug/m^3	<6	
DIBENZO(a,h)ANTHRACENE	53-70-3	6 ug/m^3	<6	
FLUORANTHENE	206-44-0	6 ug/m^3	<6	
FLUORENE	86-73-7	6 ug/m^3	<6	
INDENO(1,2,3-cd)PYRENE	193-39-5	6 ug/m^3	<6	
NAPHTHALENE	91-20-3	6 ug/m^3	<6	
PHENANTHRENE	85-01-8	6 ug/m^3	<6	
PYRENE	129-00-0	6 ug/m^3	<6	

MDL = Minimum Detection Limit.

Calculated on a wet weight basis

Michael Veraldi

Michael Veraldi-Laboratory Director

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Table 1 MW: Table 1 CAS: Table 2 RTECS: Table 2

METHOD: 5515, Issue 2	**EVALUATION:** PARTIAL	**Issue 1:** 15 May 1985 **Issue 2:** 15 August 1994

NIOSH: Table 3
OSHA :

PROPERTIES: Table 1

COMPOUNDS: acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, benzo[e]pyrene, chrysene, dibenz[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, pyrene

SYNONYMS: PAH; PNA; also see Table 2.

SAMPLING

SAMPLER: FILTER + SORBENT (2-µm, 37-mm PTFE + washed XAD-2, 100 mg/50 mg)

FLOW RATE: 2 L/min

VOL-MIN: 200 L
-MAX: 1000 L

SHIPMENT: transfer filters to culture tubes; wrap sorbent and culture tubes in Al foil; ship @ 0 °C

SAMPLE STABILITY: unknown; protect from heat and UV radiation

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 6 to 10

AREA SAMPLES: 8 replicates on preweighed filters for solvent selection

ACCURACY

RANGE STUDIED, ACCURACY, BIAS, and OVERALL PRECISION ($\hat{S}_{rT}$): not measured

MEASUREMENT

METHOD: GAS CHROMATOGRAPHY, CAPILLARY COLUMN, FID

ANALYTE: compounds above

EXTRACTION: 5 mL organic solvent appropriate to sample matrix (step 7)

INJECTION VOLUME: 4 µL; 10:1 split

COLUMN: 30 m x 0.32-mm ID, fused silica capillary, 1-µm DB-5

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 250 °C
-PROGRAM: 130 to 290 °C @ 4 °C/min

GASES-CARRIER: He @ 1 mL/min
-MAKEUP: He @ 20 mL/min

LOD: ca. 0.3 to 0.5 µg per sample [1]

CALIBRATION: external standards in toluene

RANGE, LOD, and PRECISION ($\bar{S}_r$): EVALUATION OF METHOD

APPLICABILITY: The working range for B[a]P is 3 to 150 µg/m^3 for a 400-L air sample. Specific sample sets may require modification in filter extraction solvent, choice of measurement method, and measurement conditions.

INTERFERENCES: Any compound which elutes at the same GC retention time may interfere. Heat, ozone, NO_2, or UV light may cause sample degradation.

OTHER METHODS: This revises P&CAM 183 [2]. The spectrophotometric methods, P&CAM 184 and 186 [2], have not been revised. Method 5506 (HPLC) uses the same sampling technique and is more sensitive.

REAGENTS:

1. Filter extraction solvent: acetonitrile, benzene,* cyclohexane, methylene chloride,* or other appropriate solvents, pesticide grade (step 7).
2. Toluene, pesticide grade.
3. Water, distilled, deionized.
4. PAH reference standards,* appropriate to the PAH-containing matrix sampled.
5. Calibration stock solution, 0.25 mg/mL.* Check purity of each PAH reference standard by GC/FID, HPLC/fluorescence and/or melting point. Purify, if necessary, by recrystallization. Weigh 25 mg of each PAH into a 100-mL volumetric flask; dilute to volume with toluene. Stable six months if refrigerated and protected from light.
6. Helium, prepurified.
7. Hydrogen, dry.
8. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter. PTFE-laminated membrane filter, 2-μm pore size, 37-mm diameter (Gelman Zefluor, Membrana, Pleasantown, CA, or equivalent), backed by a spacer (37-mm OD, 32-mm ID) cut from a cellulose support pad or SKC #225-23, in cassette filter holder.
      NOTE 1: If sampling is to be done in bright sunlight, use opaque or foil-wrapped cassettes to prevent sample degradation.
      NOTE 2: Take filters to be preweighed from the filter package and allow to equilibrate 24 h with laboratory atmosphere before taring.
   b. Sorbent tube, connected to filter with minimum length PVC tubing. Plastic caps are required after sampling. Washed XAD-2 resin (front = 100 mg; back = 50 mg) (Supelco ORBO 43 or equivalent). Pressure drop at 2 L/min airflow 1.6 to 2 kPa (15 to 20 cm H_2O).
2. Personal sampling pump capable of operating for 8 h at 2 L/min, with flexible connecting tubing.
3. Aluminum foil.
4. Vial, scintillation, 20-mL, glass, PTFE-lined cap.
5. Refrigerant, bagged.
6. Culture tubes, PTFE-lined screw cap, 13-mm x 100-mm.
7. Forceps.
8. Filters, 0.45-μm, PTFE (for filtering sample solutions).
9. Pipet, 5-mL.
10. Syringes or micropipets, 1- to 100-μL.
11. Ultrasonic bath.
12. Gas chromatograph with FID, electronic integrator, and capillary column (page 5515-1).
13. Volumetric flasks, 10- and 100-mL.
14. Lighting in laboratory: incandescent or UV-shielded fluorescent.

SPECIAL PRECAUTIONS: Treat benzene, methylene chloride, and all polynuclear aromatic hydrocarbons as carcinogens. Neat compounds should be weighed in a glove box. Spent samples and unused standards are toxic waste. Regularly check counter tops and equipment with "black light" for fluorescence as an indicator of contamination by PAH.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Take personal samples at 2 L/min for a total sample size of 200 to 1000 L. Take a concurrent set of eight replicate area samples at 2 to 4 L/min on preweighed, 2-µm PTFE filters in an area of highest expected PAH concentration.
   NOTE: The area samples are needed for solvent selection (step 7).
3. Immediately after sampling, transfer the filter carefully with forceps to a scintillation vial. Hold filter at edge to avoid disturbing the deposit. Cap the scintillation vial and wrap it in aluminum foil.
   NOTE: This step is necessary to avoid loss of analytes due to sublimation and degradation by light.
4. Cap the sorbent tube and wrap it in aluminum foil.
5. Ship to laboratory in insulated container with bagged refrigerant.

SAMPLE PREPARATION:

NOTE: UV light may degrade PAH. Use yellow, UV-absorbing shields for fluorescent lights or use incandescent lighting.

6. Refrigerate samples upon receipt at laboratory.
7. Determine optimum extraction solvent.
   a. Allow the preweighed area filter samples to equilibrate 24 h with the laboratory atmosphere.
   b. Weigh the area filters. Determine total weight collected on each.
   c. Extract the first pair of area filters with acetronitrile, the second with benzene, the third with cyclohexane, and the fourth with methylene chloride, according to step 8.
      NOTE: Use alternate solvents, if appropriate. PAH of interest may be entrained within, and adsorbed by, particulate matter collected on the filter. It is necessary to determine the solvent which maximizes recovery of the PAH from each sample matrix. For example, methylene chloride [3,4] and benzene:ethanol (4:1 v/v) [5] have been recommended for extraction of PAH from diesel exhaust particulate.
   d. Analyze the extracts for the PAH of interest (steps 10 through 18). Normalize the total mass of PAH found to the mass of sample collected.
   e. Choose the solvent which gives the highest recovery of PAH of interest. Use the solvent chosen to extract the personal filter samples.
8. Extract filters.
   a. Add 5.0 mL of the solvent chosen in step 7 to each scintillation vial containing a filter. Start media and reagent blanks at this step.
   b. Cap and let stand 15 to 20 min in an ultrasonic bath.
      NOTE: Soxhlet extraction may be required when large amounts of highly adsorptive particulate matter (e.g., fly ash or diesel soot) are present.
9. Desorb PAH from sorbent.
   a. Score each sorbent tube with a file in front of the primary (larger) sorbent section. Break tube at score line.
   b. Transfer front glass wool plug and front sorbent section to a culture tube. Transfer back

sorbent section and the middle glass wool plug to a second culture tube.
c. Add 5.0 mL toluene to each culture tube. Cap the culture tubes.
d. Allow samples to stand for 30 min. Swirl occasionally.

10. Filter all sample extracts through an 0.45-µm membrane filter.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards.
    a. Dilute aliquots of calibration stock solution with toluene in 10-mL volumetric flasks (e.g., to 5, 1, 0.2, 0.05, and 0.005 µg/mL).
    b. Intersperse working standards and samples in the measurements.
    c. Prepare calibration graphs (peak area vs. µg of each PAH per sample).
12. Recovery and desorption efficiency.
    a. Determine recovery (R) from filters and desorption efficiency (DE) from sorbent tubes at least once for each lot of filters and sorbent tubes used in the range of interest.
       (1) Filters. Using a microliter syringe or micropipette, spike four filters at each of five concentration levels with calibration stock solution. Allow the filters to dry in the dark overnight. Analyze the filters (steps 8, 10, and 14 through 16). Prepare graphs of R vs. amounts found.
       NOTE: This step may not be used for some highly adsorptive particulate matrices for which calibration by the method of standard additions may be more accurate.
       (2) Sorbent tubes. Transfer an unused front sorbent section to a culture tube. prepare a total of 24 culture tubes in order to measure DE at five concentration levels plus blanks in quadruplicate. Using a microliter syringe or micropipette, add calibration stock solution directly to sorbent. Cap culture tubes and allow to stand overnight in the dark. Analyze (steps 9, 10, and 14 through 16). Prepare graphs of DE vs. amounts found.
    b. Check R and DE at two levels for each sample set, in duplicate. Repeat determination of R and DE graphs if checks do not agree to within ±5% of DE graph.
13. Analyze at least three field blanks for each sample medium.

MEASUREMENT:

14. Set GC according to manufacturer's recommendations and to the conditions on page 5515-1.
15. Inject sample aliquot. Start temperature program.
16. Measure peak areas.
    NOTE 1: Approximate retention times appear in Table 4.
    NOTE 2: If peak area is above the calibration range, dilute with appropriate solvent, reanalyze, and apply dilution factor in calculations.
    NOTE 3: If sample has many interferences, additional sample cleanup may be necessary. Many cleanup procedures have been published. Liquid-liquid partitioning between cyclohexane and nitromethane [6,7] is widely used, but other techniques may be more appropriate for specific samples.

CALCULATIONS:

17. Read the mass, µg (corrected for R or DE) of each analyte found on the filter (W) and front sorbent (W_f) and back sorbent (W_b) sections, and on the average media blank filter (B) and front sorbent (B_f) and back sorbent (B_b) sections from the calibration graphs.
18. Calculate concentration, C (mg/m^3), in air as the sum of the particulate concentration and the vapor concentration using the actual air volume sampled, V (L).

$$C = \frac{(W - B + W_f + W_b - B_f - B_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Owing to large interferences that occured while utilizing NIOSH Method P&CAM 206 for samples collected during asphalt roofing operations, the gas chromatographic capillary column method was developed. The GC method has been evaluated using several hundred field filter and sorbent tube sampling trains. To date, no statistical studies have been initiated. Overall, standard spiked filters and sorbent tubes have yielded reproducible measurement calibration graphs. The method has been applied to the following sources with semi-quantitative results using three separate particulate extraction solvents (benzene, cyclohexane, acetonitrile): aluminum reduction facilities, asphalt fume, coal gasification plants, coal liquefaction plants, coal tar pitch, coke oven emissions, creosote treatment facilities, diesel exhaust, graphite electrode manufacturing, petroleum pitch, and roofing tearoff operations.

REFERENCES:

[1] UBTL, Inc., NIOSH Sequence #4220-O (NIOSH, unpublished, August 10, 1984).

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 1, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[3] Breuer, G. M. Anal. Lett., 17 (A11), 1293-1306 (1984).

[4] Zweidinger, R. B., S. B. Tejada, D. Dropkins, J. Huisingh, and L. Claxton. "Characterization of Extractable Organics in Diesel Exhaust Particulate," paper presented at Symposium on Diesel Particulate Emissions Measurement Characterization, Ann Arbor, MI (1978).

[5] Swarin, S. J. and R. L. Williams. "Liquid Chromatographic Determination of Benzo[a]pyrene in Diesel Exhaust Particulate: Verification of the Collection and Analytical Methods," Polynuclear Aromatic Hydrocarbons: Physical and Biological Effects, Bjorseth, A. and Dennis, Eds., Battelle Press, pp. 771-790 (1980).

[6] Wise, S. A., et al. "Analytical Methods for the Determination of Polycyclic Aromatic Hydrocarbons on Air Particulate Matter," Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry, Cooke, Dennis and Fisher, Eds., Battelle Press, pp. 919-929 (1982).

[7] Novotny, M., M. L. Lee and K. D. Bartle. J. Chromatog. Sci., 12, 606-612 (1974).

[8] Backup Data Report for Method 5506, Analytical Report for NIOSH Sequence 4170 (NIOSH, DPSE, MRSB, unpublished, March 16, 1984).

[9] Studt., P., Liebigs Ann. Chem., 528 (1978).

[10] Clar, E. Polycyclic Hydrocarbons, Academic Press (1964).

[11] Handbook of Chemistry and Physics, 62nd ed., CRC Press (1982).

[12] Beilstein 5 (1), 344.

METHOD REVISED BY:

B.R. Belinky, NIOSH/DPSE, and E.J. Slick; J.C. Holt, D.E. Bilak, and J.B. Perkins, DataChem Laboratories, Inc., Salt Lake City, UT.

Table 1. Formulae and physical properties.

COMPOUND (by M.W.)	EMPIRICAL FORMULA	MOLECULAR WEIGHT	MELTING POINT (°C)*	BOILING POINT (°C)*	REF.
1. NAPHTHALENE	$C_{10}H_8$	128.17	80.2	218	[10]
2. ACENAPHTHYLENE	$C_{12}H_8$	152.20	92-93	265-275	[11]
3. ACENAPHTHENE	$C_{12}H_{10}$	154.21	96.2	279	[11]
4. FLUORENE	$C_{13}H_{10}$	166.22	116	293-295	[10]
5. ANTHRACENE	$C_{14}H_{10}$	178.23	218	340	[10]
6. PHENANTHRENE	$C_{14}H_{10}$	178.23	100	340	[10]
7. FLUORANTHENE	$C_{16}H_{10}$	202.26	110	384*	[10], [12]
8. PYRENE	$C_{16}H_{10}$	202.26	156	393	[10]
9. BENZ[a]ANTHRACENE	$C_{18}H_{12}$	228.29	162-167	435	[10]
10. CHRYSENE	$C_{18}H_{12}$	228.29	255-256	448	[10]
11. BENZO[b]FLUORANTHENE	$C_{20}H_{12}$	252.32	168	--	[10]
12. BENZO[k]FLUORANTHENE	$C_{20}H_{12}$	252.32	217	480	[11]
13. BENZO[a]PYRENE	$C_{20}H_{12}$	252.32	179	495	[10]
14. BENZO[e]PYRENE	$C_{20}H_{12}$	252.32	178-179	--	[10]
15. BENZO[ghi]PERYLENE	$C_{22}H_{12}$	276.34	273	--	[10]
16. INDENO[1,2,3-cd]PYRENE	$C_{22}H_{12}$	276.34	161.5-163	530	[9]
17. DIBENZ[a,h]ANTHRACENE	$C_{22}H_{14}$	278.35	267	524	[10]

*Many of these compounds will sublime.

Table 2. Synonyms.

COMPOUND (alphabetically)	SYNONYMS
1. ACENAPHTHENE	CAS# 83-32-9; RTECS# AB1000000
2. ACENAPHTHYLENE	CAS# 208-96-8; RTECS# AB1254000
3. ANTHRACENE	CAS# 120-12-7; RTECS# CA9350000
4. BENZ[a]ANTHRACENE	1,2-benzanthracene; benzo[b]phenanthrene; 2,3-benzophenanthrene; tetraphene; CAS# 56-55-3; RTECS# CV9275000
5. BENZO[b]FLUORANTHENE	3,4-benzofluoranthene; 2,3-benzofluoranthene; benz[e]acephenanthrylene; B[b]F; CAS # 205-99-2; RTECS# CU1400000
6. BENZO[k]FLUORANTHENE	11,12-benzofluoranthene; CAS# 207-08-9; RTECS# DF6350000
7. BENZO[ghi]PERYLENE	1,12-benzoperylene; CAS# 191-24-2; RTECS# DI6200500
8. BENZO[a]PYRENE	3,4-benzopyrene; 6,7-benzopyrene; B[a]P; BP; CAS# 50-32-8; RTECS# DJ3675000
9. BENZO[e]PYRENE	1,2-benzopyrene; 4,5-benzopyrene; B[e]P; CAS# 192-97-2; RTECS# DJ4200000
10. CHRYSENE	1,2-benzophenanthrene; benzo[a]phenanthrene; CAS# 218-01-9; RTECS# GC0700000
11. DIBENZ[a,h]ANTHRACENE	1,2,5,6-dibenzanthracene; CAS# 53-70-3; RTECS# HN2625000
12. FLUORANTHENE	benzo[jk]fluorene; Idryl; CAS# 206-44-0; RTECS# LL4025000
13. FLUORENE	o-biphenylenemethane; CAS# 86-73-7; RTECS# LL5670000
14. INDENO[1,2,3-cd]PYRENE	2,3-phenylenepyrene; CAS# 193-39-5; RTECS# NK9300000
15. NAPHTHALENE	naphthene; CAS# 91-20-3; RTECS# QJ0525000
16. PHENANTHRENE	CAS# 85-01-8; RTECS# SF7175000
17. PYRENE	benzo[def]phenanthrene; CAS# 129-00-0; RTECS# UR2450000

Table 3. Exposure Limits.

COMPOUND (alphabetically)	OSHA	NIOSH	ACGIH
1. ACENAPHTHENE	--	--	--
2. ACENAPHTHYLENE	--	--	--
3. ANTHRACENE	0.2 mg/m^3	--	--
4. BENZ[A]ANTHRACENE	--	--	--
5. BENZO[B]FLUORANTHENE	--	--	suspect carcinogen
6. BENZO[K]FLUORANTHENE	--	--	--
7. BENZO[GHI]PERYLENE	--	--	--
8. BENZO[A]PYRENE	0.2 mg/m^3 (benzene sol.)	0.1 mg/m^3 (cyclohexane sol.)	suspect carcinogen
9. BENZO[E]PYRENE	--	--	--
10. CHRYSENE	0.2 mg/m^3 (benzene sol.)	lowest feasible, carcinogen	suspect carcinogen
11. DIBENZ[A,H]ANTHRACENE	--	--	--
12. FLUORANTHENE	--	--	--
13. FLUORENE	--	--	--
14. INDENO[1,2,3-CD]PYRENE	--	--	--
15. NAPHTHALENE	10 ppm	10 ppm; STEL 15 ppm	10 ppm; STEL 15 ppm
16. PHENANTHRENE	0.2 mg/m^3	--	--
17. PYRENE	--	--	--

Table 4. Approximate PAH retention times.

COMPOUND	RETENTION TIME (min)*
1. NAPHTHALENE	not available
2. ACENAPHTHALENE	7.66
3. ACENAPHTHENE	8.37
4. FLUORENE	10.5
5. PHENANTHRENE	15.0
6. ANTHRACENE	15.3
7. FLUORANTHENE	21.4
8. PYRENE	22.6
9. BENZ[a]ANTHRACENE	29.4
10. CHRYSENE	29.6
11. BENZO[e]PYRENE	36.4
12. BENZO[b]FLUORANTHENE	35.1
13. BENZO[k]FLUORANTHENE	35.2
14. BENZO[a]PYRENE	36.2
15. DIBENZ[a,h]ANTHRACENE	43.9
16. BENZO[ghi]PERYLENE	45.6
17. INDENO[1,2,3-cd]PYRENE	43.6

*NOTE: Actual retention times will vary with individual columns and column age.

[redacted]

[redacted]

[redacted]

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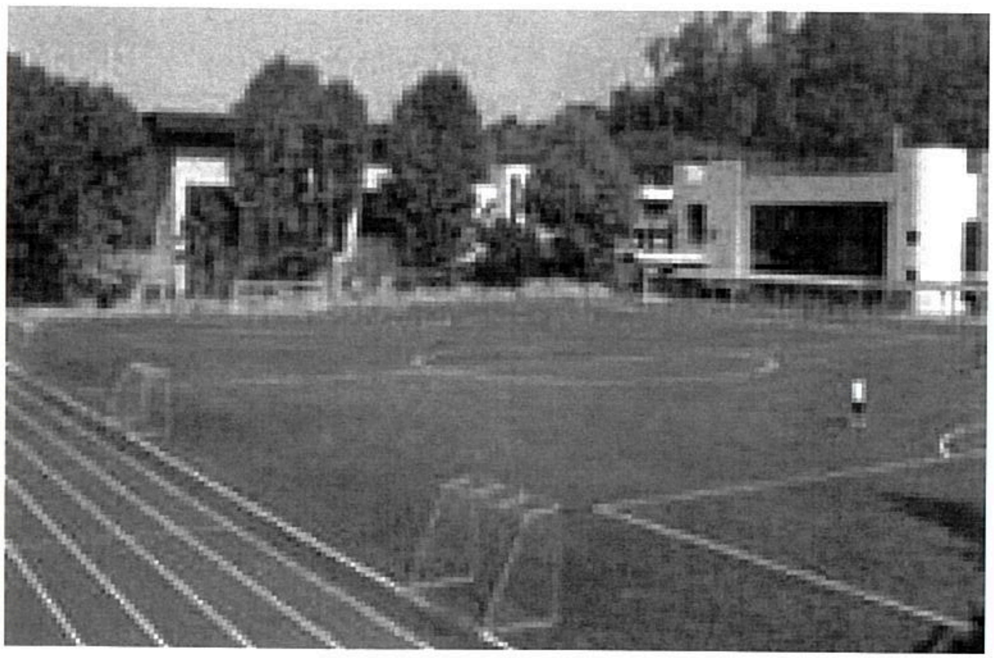
[redacted]

Assessing the Health and Environmental Impact from the Use of End-of-Life Tire Rubber Crumb as Artificial Turf in Sports Arenas



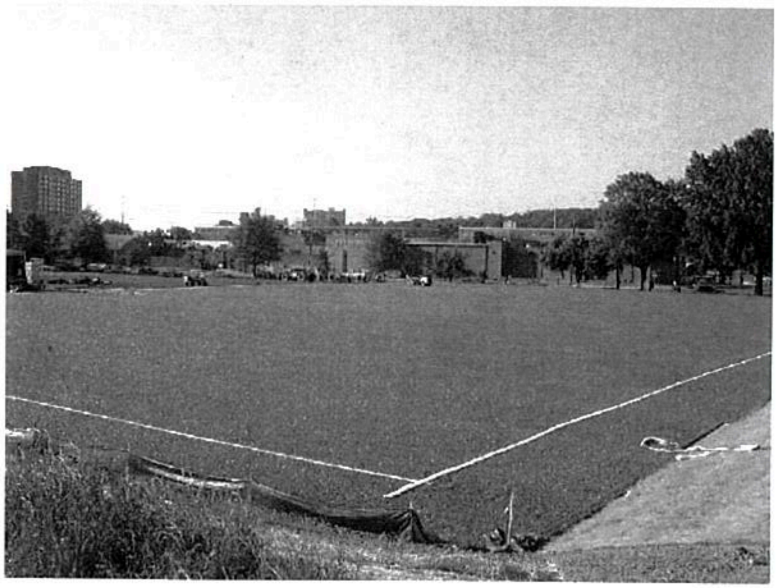
D.A. Birkholz

Director, Research and Development

ALS Laboratory Group

Edmonton, Alberta

Benefit of Artificial Turf



The artificial turf installed at Gunston is filled with rubber granules that ***prevent compaction and dangerous playing field conditions. It is a safer field that is easier on player knees and ankle joints.***

ASA Board member Mac Brown noted, "***<u>This stuff plays like a great grass field, but does not die from overuse.</u>***"

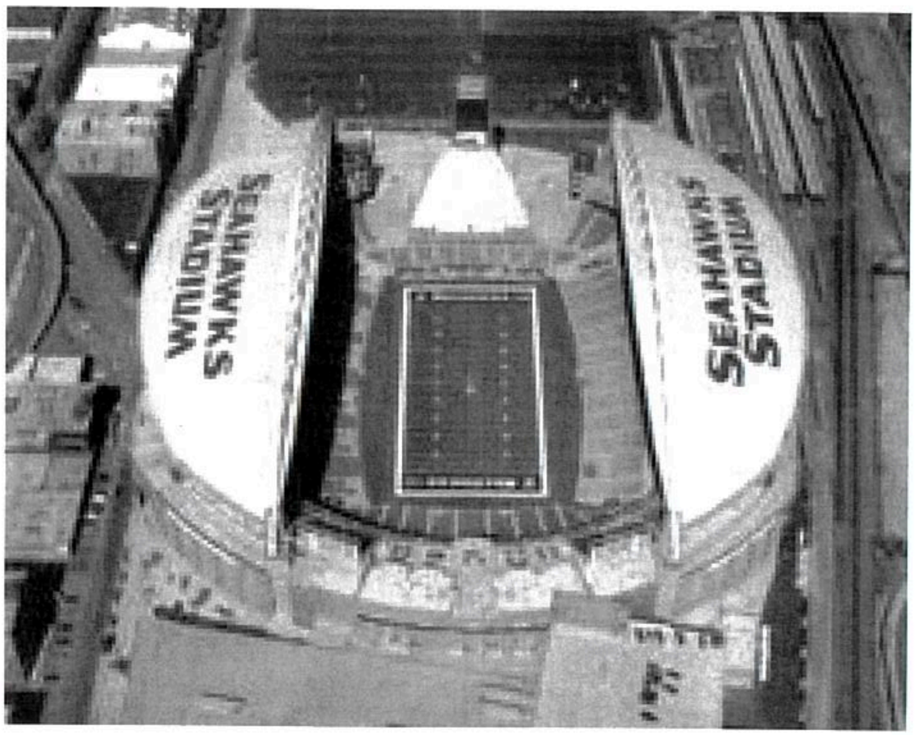
The synthetic surface allows ***<u>unlimited play with low maintenance and predictable, grass-like performance</u>***. The field has an underground field drainage systems that keeps the field playable in almost all weather conditions.

Benefits of Artificial Turf

The Artificial Turf Field is ***ideal for football, field hockey and soccer games and practices***

University of Alberta Faculty of Physical Education and Recreation

Benefit



<u>Artificial turf requires no mowing, watering, fertilizing, or re-seeding. Regular maintenance involves brushing and occasional vacuuming using leased, rented or loaned equipment.</u>

The typical sand-based soccer/football field can use between 2.5 million and 3.5 million gallons of water per year in the Pacific Northwest. Coupled with reduced labor costs related to maintenance, equipment and eliminated costs for supplies such as fertilizers, herbicides, and pesticides, several of our clients ***<u>have seen a reduction in maintenance costs of as much as $30,000 to $60,000 per field, per year</u>***.

Tire Crumb - Benefit

As for the tire crumb product, several potential advantages exist in its use as a playground surface amendment. Although most discarded tires are *placed into landfills to degrade slowly, economic use of tire crumb diverts old tires from landfills and piles where they present serious hazards. Stockpiled tires in landfills can contribute to fires that are difficult to extinguish, releasing combustion products (e.g., benzene, other volatile organic hydrocarbons, and dioxins) into the air. The hollow structure of a tire creates a breeding space for human disease vectors.* Advantages are that the crumb product is lightweight and cost-effective according to school district users. The manufacturer claims that the product has a superior degree of cushioning against falls, the main purpose of its use below play structures. Direct application is simple and cheap, much like that of sand: Simply shovel it into place.

Concerns raised over turf use in indoor facilities

- Exposure to ***carcinogenic*** PAHs, amines and N-nitrosamines –skin contact and ingestion
- Odour
- ***Breathing in toxic chemicals*** including fine rubber material
- ***Leaching of toxic chemicals*** with concomitant release to environment
- ***Abrasion of surfaces with use and concomitant release of particulates*** and toxic chemicals
- Increase incidence of methycillin resistant ***Staphylococcus aureus***
- Exposure to toxins produced by fungus, alga, and mould
- Foot blisters
- ***Latex allergy and asthma***
- Fire hazards

Concerns raised

A study of particulate air pollutants in Denver, Colorado, found ***black respirable particulates*** that were identified as ***airborne tire fragments***

suggest that these respirable "tire dust" particles ***may contribute to the pathogenesis of lung diseases related to air pollution***. Whether respirable particles are created during regular use of the tire crumb product requires further investigation, given that a high amount of energy is required to create smaller crumb rubber particles. Reports of haze while children played on the applied product may or may not be related.

Mitigating studies – Tire crumb in playgrounds

Anderson et al, ***2006*** – Environ. Health Perspectives

Group of physicians including Dr. Tee Guidotti

Reviewed scientific evidence and literature

Concluded that ***rubber crumb covering for play areas presents a very low risk for both children and environment***

Mitigating Studies

- ***<u>Norwegian Institute for Water Research, 2005</u>***
- Based upon study of the concentrations and leaching potential of hazardous chemicals used in artifical turf pitches
- <u>Greatest environmental risk linked to the leaching of chemicals through surface water run-off in connection with precipitation</u>
- Assessment shows there is a risk of environmental effects in both the water phase and sediment
- Zinc, alkylphenols and octylphenol ***<u>predicted</u>*** to exceed the limits for environmental effects
- The total annual amounts of hazardous substances leaching from a normal sports ground are fairly low which means that any environmental effects are expected to be local only
- Leachate generated by shaking 1 kg of material (fiber or rubber granulate) in 10 litres of water for 24 h.
- PNEC taken from EU's risk assessment documents, ***<u>no actual measure of toxicity</u>***
- <u>PAHs and phthalates found in leachate but not considered problematic</u>

Mitigating Studies

- ***Norwegian Institute of Public Health and the Radium Hospital, January 2006***
- An assessment of the ***health risks for football players playing in sports halls with artificial turf pitches***
- Nine exposure scenarios were used: adults, juniors, older children and children
- ***Exposure routes assessed: inhalation exposure, skin exposure and oral exposure***
- Chemicals assessed include: VOCs (234 chemicals measured, 29 identified), PCBs, PAHs, phthalates, alkylphenols. ***Used highest analysis values in regards to recycled rubber granulate.***
- Adults ¤ 20 years
- Juniors 16 – 19 years
- Older children 12 – 15 years
- Children 7 – 11 years

Mitigating Studies

Conclusions: *Norweigian study*

The use of artificial turf halls does not cause any elevated health risk. This applies to children, older children, juniors and adults

Higher values of VOC were measured than are normally found in homes. It was concluded that the values which were measured for total VOC do not constitute any elevated health risk *but knowledge of this area is inadequate.*

As regards allergies, it is concluded that exposure to the low concentrations which were measured does not constitute any elevated risk with respect to the development of contact allergies.

The possibility that the use of car tires could cause exposure to latex allergens and thus lead to the development of airway allergies cannot be entirely eliminated

Studies have been carried out which indicate a link between exposure to phthalates and the development of asthma/allergies. At the present time, it is not possible to carry out a risk assessment in this area because of a lack of available knowledge.

Mitigating studies

Norwegian study

Training in sports halls does not cause any increased risk of leukemia as a result of benzene exposure or any elevated risk as a result of exposure to PAHs

On the basis of the exposures which have been calculated in connection with the use of indoor halls with artificial turf in which recycled rubber granulate is used, ***there is no evidence to indicate that the use of such halls causes an elevated health risk***.

Reservation with respect to the development of asthma/airway allergens as no information is available on the occurrence of latex allergens in hall air.

Mitigating Studies

Norwegian Building Research Institute, 2004

Study covers a total of ***four types of rubber granulate and two types of artificial turf fibre.***

The rubber granulates and artificial turf fibres were analysed with regard to the total content of arsenic, cadmium, copper, chromium, mercury, nickel, zinc, PCB, PAH, phthalates, and phenols

Leachate tests and degassing tests were also carried out.

The results are compared with Norwegian and foreign limits for soil and water

The aim of this project was to give a satisfactory fingerprint of potentially hazardous substances for soil, air, water and humans linked to the use of rubber granulate in artificial turf systems.

Mitigating Studies

Norwegian Building Research Institute, 2004

- Leachate was 10L/kg at 10 RPM for 24 h
- For the degassing test, 2 g of rubber granulate was heated to 70^{o}C for 30 minutes before gas mixture was analysed

- ***Findings***

- Artificial turf fibers contain Cu, Zn, phthalates, 4-t-octylphenol and iso-nonylphenol. Zn and Cu levels comply with normative values for sensitive land use
- Leachate contained Zn and exceeded WQ guidelines but levels lower than Canadian DW guidelines.

Mitigating studies

Norwegian Building Research Institute

Rubber granulates contain Pb, Cd, Cu, Hg, Zn, PAHs, phthalates, and alkylphenols

Pb, Cd, Cu, and Hg below normative values for most sensitive land use

Zn and PAH in the recycled rubber granulates exceed values for the most sensitive land use

Dibutylphthalate and diisononlyphthalate exceed PNEC for terrestrial life taken from the EU program for risk assessment

Isononlphenol is above Canadian Environ. Quality guidelines for cultivated land

Leachate conc. anthracene, fluoranthene, pyrene, and nonlyphenols exceed Can. Environ. Quality guidelines for freshwater

An expanded risk assessment with an analysis of possible spreading paths and changes in leaching properties over time is necessary to determine the degree to which the conc. Of Zn, anthracene, fluoranthene, pyrene, phthalates, and nonylphenols in the leachate are actually harmful to people and the environment.

Mitigating studies

Norwegian Building Research Institute

Recycled rubber granulates ***give off significant number of alkylated benzenes in gaseous form. Trichloromethane and cis-1,2-dichloroethene were also found***

It is recommended that measurements be taken of air quality above pitches be taken to determine whether the air quality is satisfactory.

Mitigating Studies

Norwegian Institute for Air Pollution, 2005

Measured concentrations of ***airborne dust and gas phase compounds in indoor air in indoor artificial turf pitches***

Measurements taken in a hall with recently laid rubber granulate (styrene butadiene rubber, SBR) which had been in use for one year.

Mitigating studies

Ostfoldhallen has airborne dust concentrations that one would expect in an indoor environment for both PM10 and PM2.5

Manglerudhallen and Valhall have ***elevated levels of PM 2.5 and are close to the national recommended norm of 20 ug/m^3***

Airborne dusts in Manglerudhallen and Valhall ***contain large quantities of rubber from the granulate,*** whilst in Ostfoldhallen the proportion of rubber from the granulate is considerably less

In all three halls the proportion of organic material is considerable

The ***airborne dust contains PAHs, phthalates, semi-volatile organic compounds, benzothiazoles and aromatic amines***

Mitigating studies

- Total VOC levels ***without ventilation in Manglerudhallen could reach very high levels***
- Component spectrum has a ***clear signature from rubber granulate and contains components which are associated with adverse effects on health***
- TVOC in Valhall is high.
- Measurements taken show that TVOC concentrations in Manglerudhallen and Valhall are higher than in Ostfoldhallen. This means that ***there are alternative rubber granulates which give lower TVOC levels than SBR rubber.***

Problem with Studies

- Reliance on chemical analysis
- Comparison with guidelines (which vary from country to country)
- Use risk assessment which public (competitors e.g. European Seed Association) may or may not buy into depending on agenda
- Open ended statements

Toxicological evaluation for the hazard assessment of tire crumb for use in public playgrounds

Birkholz et al (2003).
J Air & Waste Mgmt Assoc

Also presented at SETAC

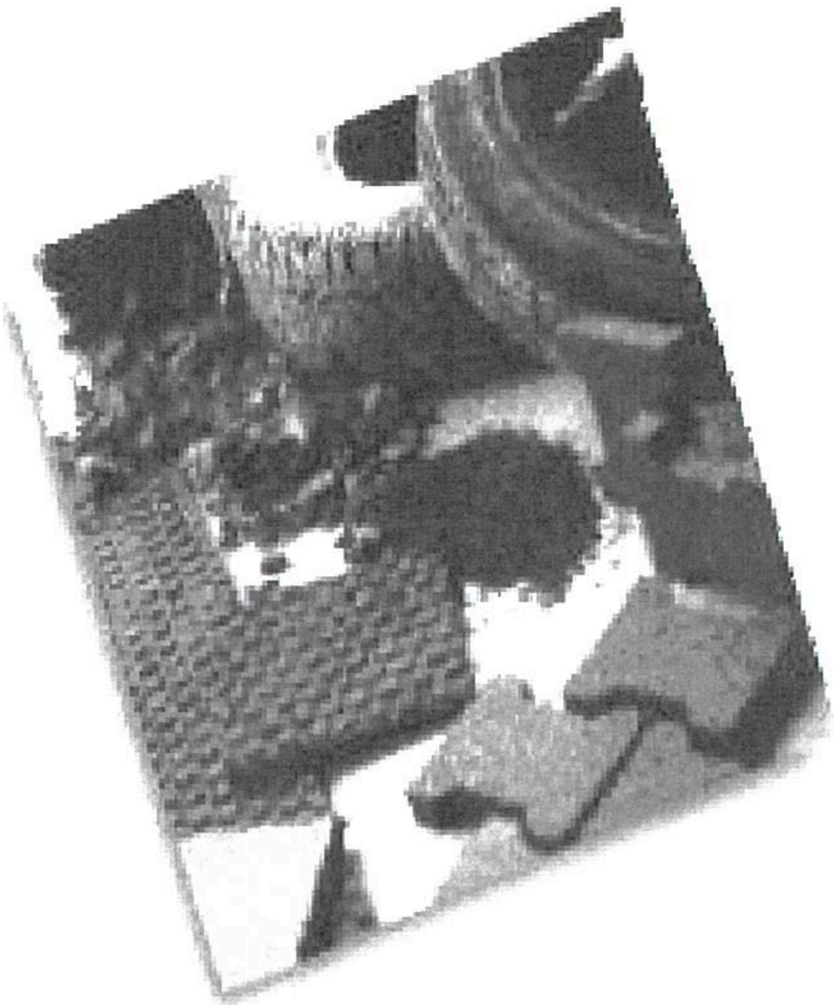
Tire Recycling

Approximately 2 million tires are generated in Alberta annually

In order to recycle 100% of spent tires, new uses will have to be found

Recycling is important to avoid situations such as the Hagarville, Ontario fire in 1990 in which a stockpile of 13 million scrap tires had burned uncontrolled

What is Tire Crumb and What Are We Proposing to Use it for?



- "Tire crumb" is crushed rubber obtained from spent vehicle tires
- Proposed use in playgrounds as a substitute for sand
- Has advantages over sand in that injuries to children such as scrapes and bruises are minimized
- Excellent way to deal with waste material, i.e. recycle used tires.

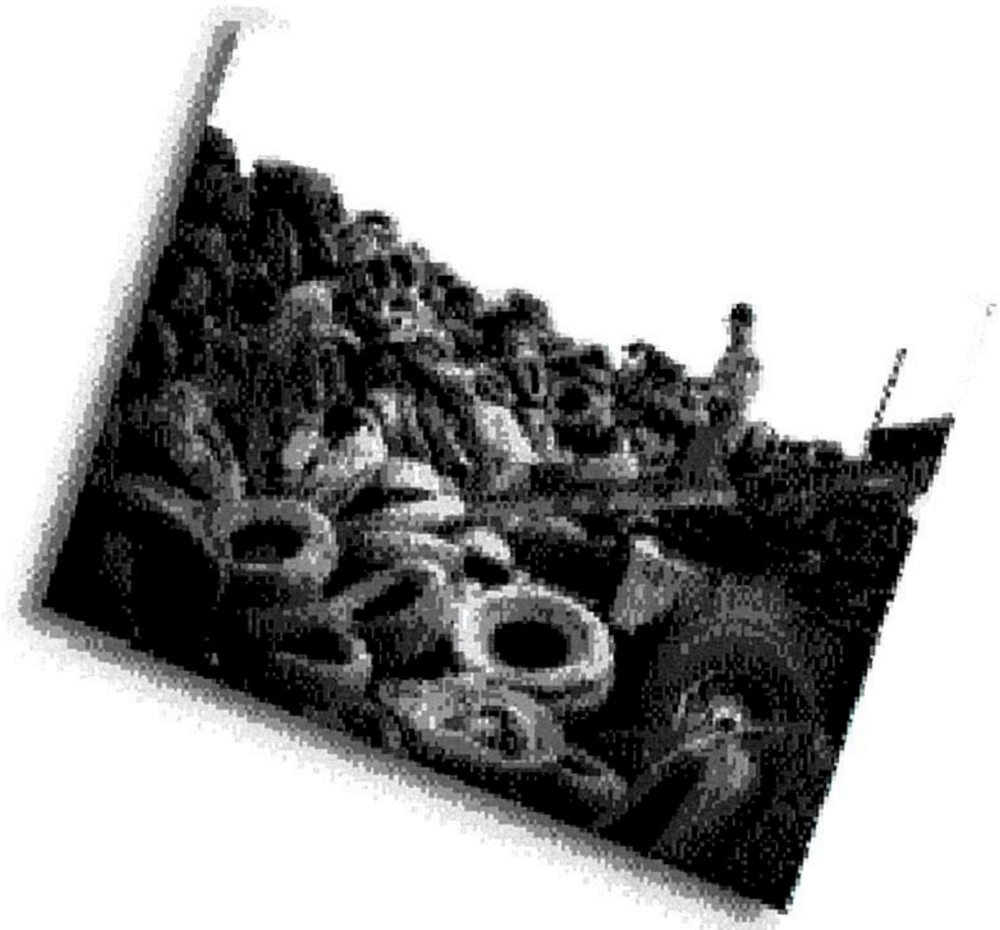
A Case Study of Tire Crumb Use on Playgrounds: Risk Analysis and Communication When Major Clinical Knowledge Gaps Exist

The stated concern relates to use of a loose, crumbled product made from used tires. ***Children playing on tire crumb could potentially be exposed by ingestion of the product directly, by ingestion of surface water runoff through the product, by inhalation of dust, or by skin contact with the material or surface water runoff.***

Concerns Over the Use of "Tire Crumb" in Playgrounds

- Human health concerns as a result of exposure of tire crumb to small children and potential exposure to toxic chemicals
- Environmental concerns as a result of potentially toxic playground runoff (rain, snowmelt) entering our storm sewers and being released to the aquatic environment

Approaches for Testing the Validity of Human Health Concerns



Exposure Assessment

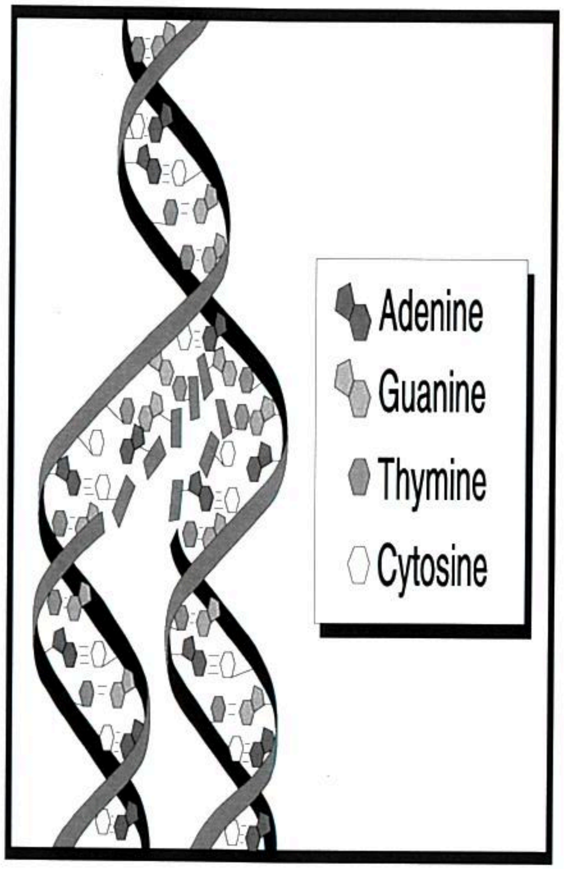
Genotoxicity testing

Methods: Exposure Assessment

Salient Features

- Risk of a toxic response to children is dependent upon exposure to chemicals which may be present in “tire crumb”
- This exposure may occur dermally (skin contact), or orally (via ingestion) and finally through inhalation of volatile constituents
- Each one of these routes of exposure was assessed in order to determine risk associated with exposure

Methods: Genotoxicity Testing

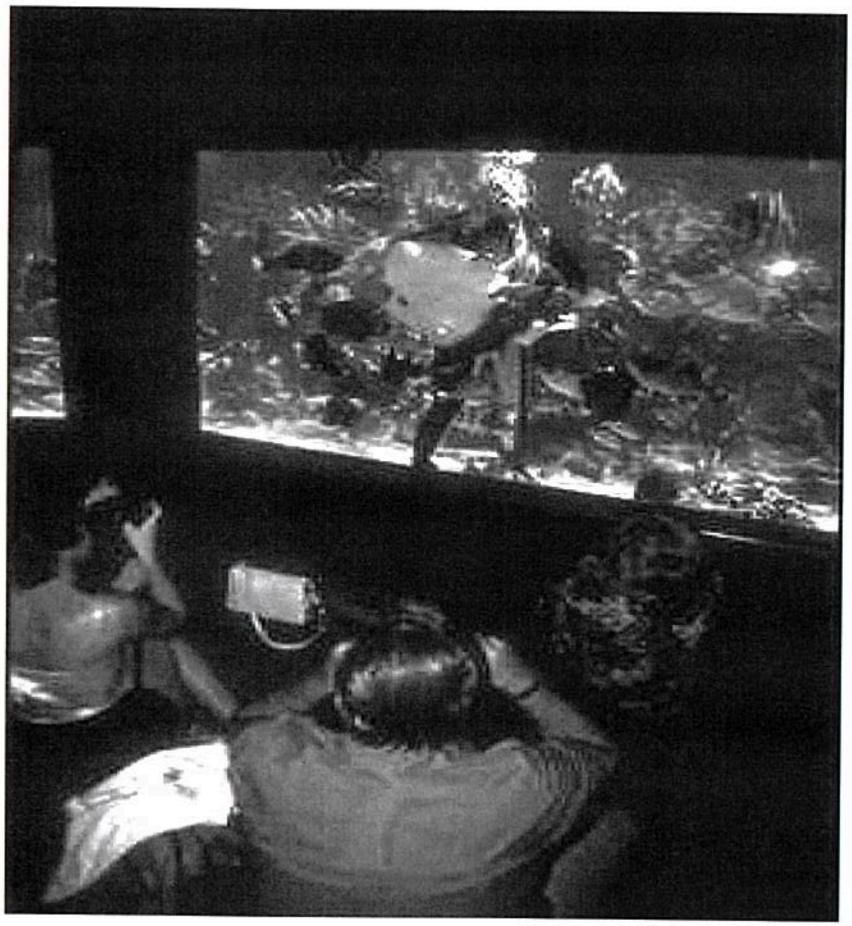


- To determine whether ingestion of small amount of "tire crumb", by small children, poses a risk with respect to exposure of chemicals which may bioaccumulate and potentially cause cancer
- Exhausative extraction (Soxhlet, 16-18h) of 200 g of "tire crumb" with dichloromethane
- Genotoxicity testing performed on the resulting extracts using: *Salmonella typhimurium* mutagenicity fluctuation assay (TA98, TA100, TA1535, TA1537) , SOS chromotest and Mutatox
- Tests conducted with and without S9 (liver homogenate)
- Extracts tested for acute lethality using Microtox to determine dilution series.
- Exchanged into DMSO: final concentrations tested were 0.24 - 2.2 mg/mL

Approaches for Testing the Validity of Environmental Concerns

- **Generate a water leachate**
- **Test with a battery of aquatic tests representative of the major trophic levels in the aquatic receiving environment**
- **If toxic, determine persistence of toxic response, i.e. generate PEEP-index**

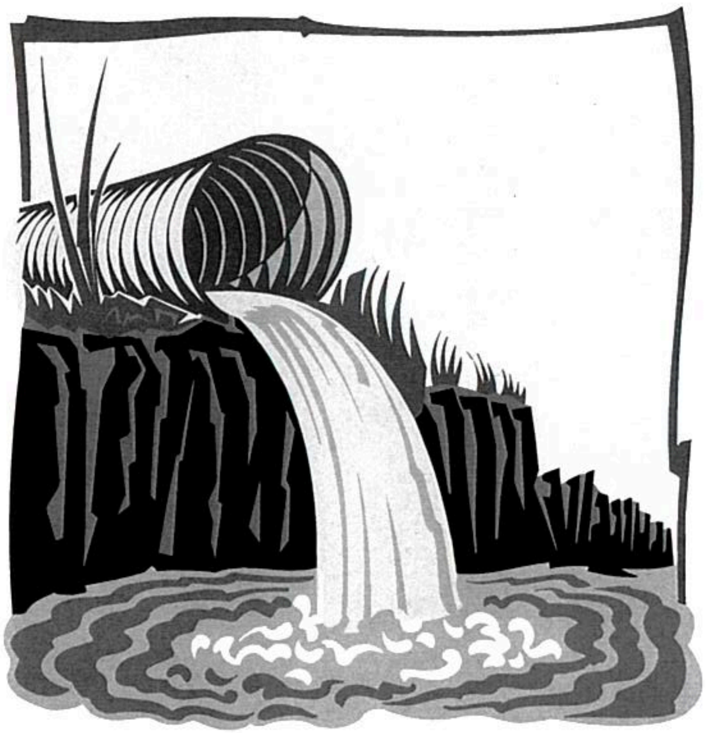
Methods



Aquatic Protection

- Generate leachate by extracting 250 g of sample with 1L of laboratory water.
- Filter leachate and test using: luminescent bacteria, invertebrates, fish and algae

Determination if toxicity is persistent



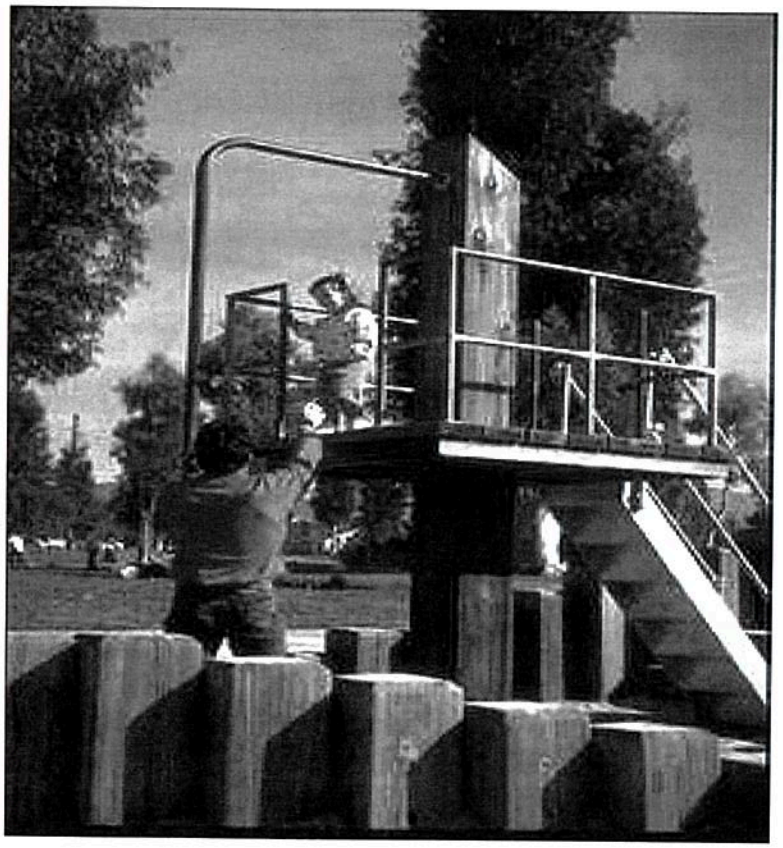
- If initial testing reveals a toxic response using aquatic organisms
  - Generate leachate by extracting 250 g of sample with 1L of laboratory water
  - Filter sample
  - Add sewage seed, nutrients and aerate filtrate for 5-days
  - Retest for toxicity using luminescent bacteria, invertebrates, fish and algae
  - Calculate PEEP-index

PEEP-index

$$PEEP\ \ index = \log\left[1 + n\left(\frac{\sum_{i=1}^{n} T_{BB} + T_{AB}}{N}\right)\right]$$

n = number of tests producing a toxic response
N = total number of tests performed (=8)
TBB = toxicity before biodegradation in TU
TAB = toxicity after biodegradation in TU

Results



EXPOSURE ASSESSMENT

“Tire crumb” does not contain chemicals with high vapour pressures, exposure via inhalation deemed low risk

Dermal exposure deemed low risk because carrier solvent is needed to extract toxic chemicals from tire crumb and to penetrate protective skin layers

Oral ingestion deemed low risk because ingestion not likely, furthermore, question of how effective stomach acids and enzymes are at extracting toxic chemicals from tire crumb and transporting them into the blood stream

Genotoxicity Testing

Sample	Ames Fluctuation Assay				SOS Test	Mutatox
	TA 98	TA 100	TA 1535	TA 1537		
	Without Liver activation					
Tire #1	NT	NT	NT	NT	NT	NT
Tire #2	NT	NT	NT	NT	NT	NT
Tire #3	NT	NT	NT	NT	NT	NT
	With Liver activation					
Tire #1	NT	MT	MT	MT	NT	NT
Tire #2	MT	NT	NT	NT	NT	NT
Tire #3	MT	MT	NT	MT	NT	NT

Results Initial Aquatic Testing

Test	Toxic Units (100/LC50 or EC50)		
	Tire Recycling #2	AB Envir R Products #1	Midwest Tire #3
Microtox	8.9	15.4	7.3
Daphnia magna	14.7	22.6	13.5
Fathead minnow	10	12.2	6.4
Alga	22.3	22	17
SUM	55.9	72.2	44.2

After Biodegradation

Test	Tire Recycling #2	AB Envir R Products #1	Midwest Tire #3
Microtox	4	10.5	5.7
Daphnia magna	1.4	6.8	1.8
Fathead minnow	<1	<1	<1
Algae	1.5	1.3	1.0
PEEP-index	1.75	1.90	1.68

Field Test: Crumb deployed in late fall, sampled in December

Test	Endpoint	AB Env. R Products #1	Crumb deployed in School
Microtox	TU	14.9	11.7
Daphnia magna	TU	16.0	8.0
Fathead minnow	TU	43.5	22.6
Algae	TU	1042	412
Cumulative toxicity	TU	1120	454
PEEP-index			3.2

Conclusions Concerning Environmental Protection

Bioassay of leachates obtained from four “tire crumb” samples revealed that all samples were toxic to all four species tested (luminescent bacteria, invertebrates, fish and green algae).

However, it was determined that the toxicity was transient, or short-term

Innoculation of “tire crumb” leachates in the laboratory with nutrients and sewage seed, followed by continuous aeration for 5-days, resulted in significant (73 - 86%) reduction in toxicity

Furthermore, bioassay of leachate samples obtained from bulk “tire crumb” before and after deployment in a school ground, revealed a 59% reduction in toxicity following short-term deployment (3 months).

These findings suggest that chemicals leaching from “tire crumb” are quickly degraded by natural processes to non-toxic forms.

In all instances except one, the PEEP-index was determined to be less than 3 which is considered to be acceptable by Environment Canada (Costan et al., 1993).

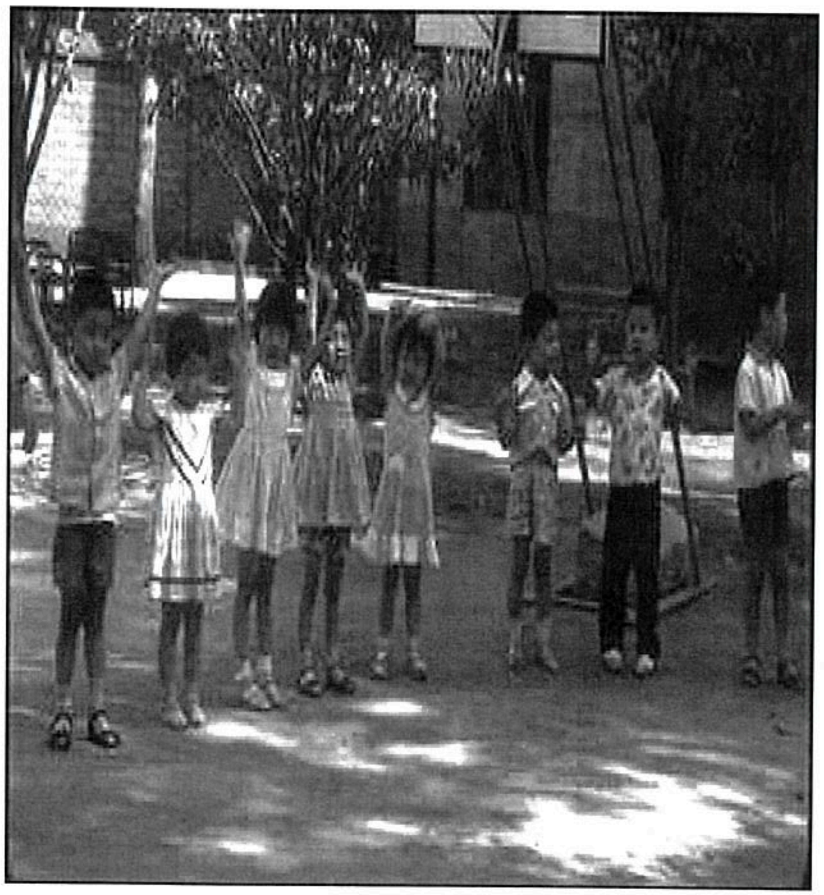
In the case of the schoolyard, the PEEP-index is marginally greater than 3 (I.e. 3.2), however, with aging this value should quickly drop to below 3.

Conclusions Concerning Human Health

An exposure assessment, performed to address the potential effects upon children playing in facilities where "tire crumb" is deployed, concluded that there was no adverse risk associated with this activity

Genotoxicity testing of "tire crumb" samples following solvent extraction concluded that no DNA-damaging or chromosome-damaging chemicals were present. This finding suggests that ingestion of small amounts of "tire crumb" by small children will not result in an unacceptable risk of contracting cancer. This finding supports the exposure assessment conclusions, particularly as it relates to oral ingestion of small amounts of "tire crumb"

Overall Conclusion



Since the impact on human health and the receiving environment is considered minimal, the benefit associated with injury control in playgrounds suggests that this use of recycled tires should be promoted and encouraged

Possible Closure

<u>Oral exposure</u> – use gastrointestinal leachate models to estimate bioavailability of chemicals taken up by digestive tract

Test using Ames mutagenicity assay and SOS-chromotest

Possibly CHEST and GJIC assays

Possible Closure

Dermal Exposure

Cyclodextrin extraction model

Ames mutagenicity test

SOS chromotest

ELISA – inhibition latex antigen test

Possible Closure

Environmental issues

Leachate (4:1 instead of 10:1)

PEEP index using variety of products and both acute and chronic toxicity tests

Possible Closure

Bacteria and toxins associated with fungus, molds, yeasts etc

Take swabs – culture and determine presence including *Staphylococcus aureus*

Possible closure

- Inhalation toxicity
- Collect PM 2.5 and PM 10
- Collect vapours (tenax, silica gel)
- Test using Ames mutagenicity, SOS-Chromosomal aberration, ELISA – inhibition latex antigen test and chemical analyses

Conclusion

- Numerous studies conducted to assess the human health and environmental impact associated with exposure to artificial turf
- Many studies based on chemical analysis and risk assessment
- Some studies done using toxicity assessments
- Despite conclusions that product is safe there is still skepticism
- It is clear that risk assessment is not readily acceptable to the public even when performed by government agencies
- Toxicological evaluations using toxicity endpoints may be more acceptable and less contentious.

TWENTY QUESTIONS ON RUBBER GRANULATE

In conjunction with the British Standards Institute (BSI), the Sports and Play Construction Association (SAPCA) is helping to prepare new European (CEN) Standards for artificial sports surfaces. Through this work SAPCA has become aware of concerns being voiced in some European countries over the use of recycled rubber from vehicle tyres in sports and play surfaces. In response SAPCA has convened a working group of UK experts to investigate the situation, and has carried out a substantial review of previous national and international studies undertaken by scientists on the risks from rubber aggregates in sporting contexts.

Dr Bryan Willoughby, an independent consultant in polymer chemistry who compiled the review, answers here some of the commonly asked questions about rubber granulate.

1. What kind of rubber granulate is used in sports and play settings?

Rubber granulate can be made from virgin or recycled (tyre) rubber. So-called Thermoplastic Elastomers (TPEs) may be used, but most granulate is vulcanised. Vulcanisation is a chemical treatment to improve the resilience and performance of raw rubber polymers.

The unique quality it adds is that whatever distortion is applied, it will always seek to recover its original shape. Nothing bounces back like a vulcanised rubber. The process also provides more consistent performance in changing temperatures.

2. So the vulcanisation process entails adding chemicals to the rubber. Are they harmful?

Few chemicals are totally benign (water can be lethal if you can't swim), and it is difficult to avoid potentially harmful chemicals when selecting to meet technical performance requirements.

But remember somebody has to handle these chemicals to make the rubber products. The challenge in rubber manufacture, as in life, is to manage the risks effectively.

There will be different chemicals for rubbers, but there may also be common ingredients.

3. Are there added chemicals in TPEs?

That will depend on the type of TPE, but certainly the chemicals of vulcanisation are not needed.

TPEs may contain fewer chemicals, but the downside is that they may not match the performance of vulcanised rubbers. Like rubbers, TPEs can be soft and flexible – but, like thermoplastics, they are prone to creep and will deform with heat.

4. Why are many rubber products black?



This is because carbon black (to the layman, 'soot') is incorporated in the rubber. Carbon black is engineered to have a controlled particle size, and the best carbon blacks can be strong reinforcing agents in rubber.

Carbon black also offers some protection from UV attack. So that means a black rubber is likely to be much stronger, tougher and longer lasting than an equivalent non-black rubber.

5. Are coloured rubber granules mechanically inferior to black rubber granules?

If we're talking about the rubbers in the granules for sports and play surfaces - tyre and Ethylene Propylene Diene Monomer (EPDM) rubbers - the answer is yes.

A coloured rubber cannot normally match the performance attainable with a black version of the same type. Whether this difference matters depends on the level of performance required.

6. What is the difference between EPDM and tyre rubbers?

Obviously, car and truck tyres are always black. The raw rubbers used in tyres are usually blends - selected to offer optimum performance in a demanding application which requires strength, fatigue and abrasion resistance.

EPDM is a general purpose rubber: it has good weathering resistance, although mechanical performance is unlikely to be a match for the tyre rubbers.

7. But tyre rubber granulate is from waste tyres – isn't this likely to be variable?

Any manufactured product is potentially variable if quality is not effectively controlled. This is true of virgin or recycled products. With rubber products, the recycler has to contend with variability in the feedstock, whereas the manufacturer of virgin rubber products has to control the mixing and vulcanisation.

How each succeeds depends on the effectiveness of their respective QA systems. Different sites may perform differently whatever the feedstock - the customer is the final judge here.

8. There are two ways of creating granulate. Is cryogenically-ground tyre granulate different from the ambient temperature product?

Both are the products of mechanical breakdown, but the cryogenic route exploits brittle fracture and gives smooth-faced granules. The ambient method tears the rubber and gives rough-faced granules. So there is a difference in the granule shape. The difference in performance in loose granulate is unclear.

9. Can the various chemicals used come out of vulcanised rubbers?

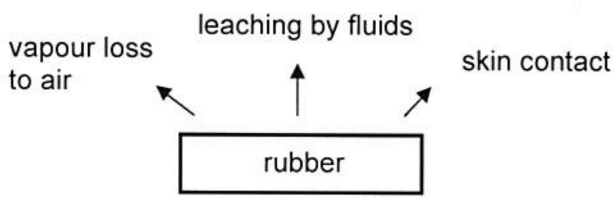
These chemicals were put in the rubber to fulfil a specific purpose, and, in the main, remain firmly locked into the rubber.

Common experience tells us this is so: rubber products do not usually feel powdery or greasy. Nor do we normally harbour concerns over familiar rubber products. Most wouldn't hesitate from handing a vulcanised rubber dummy to a baby.

Traditionally we expect rubbers to protect us from chemicals, as gloves or aprons for example, rather than introduce hazards of their own. Many rubbers make good barrier materials and tyres are expected to be substantially impermeable.

10. Trace releases must be possible – how do they occur?

If chemicals can escape, there are three possible mechanisms: volatilisation, leaching and perhaps through skin contact.



But the key word here is 'if'. Even trace migration is a selective process, and depends entirely on the prevailing conditions. Some chemicals may prove highly reluctant to leave the rubber.

11. What comes out by volatilisation?

The fact that rubbers often have a smell gives away the fact that something is volatilising. The same applies to familiar materials like leather or timber. But the nose is a very sensitive organ, and what is being released may not amount to very much.

There is also a selectivity operating within the rubber, and only the most volatile species have the opportunity to escape in this way. Research has shown this includes some impurities from the original polymerisation and some by-products of the vulcanisation and stabilisation chemistry.

Of course, a rubber in service may pick up species from the environment and re-release them subsequently.

12. Is there anything in the vapours which is harmful to health?

No doubt, given the sophistication of modern chemical analysis, a trace of something can be found which could raise concerns. But rubber is a well-established product in domestic and industrial applications, and a great many people have handled it without harmful side effects.

Remember that the first in line for exposure are those in the rubber factory who handle the freshly-vulcanised (hot) rubber. Any health concerns should have been dealt with long before the rubber reaches the consumer.

13. Is it true that Polycyclic Aromatic Hydrocarbons (PAHs), which are carcinogenic, are found in tyre rubber?

PAHs are components of aromatic process oils which provide a valuable role in processing and product performance. Grip is one thing that benefits from their presence in tyre rubbers. Not all PAHs are carcinogenic, but some certainly are.

14. Should operators and users be worried?

As with any threat, the hazard should be weighed against the risk of exposure. Here the risk is related to the chances of releasing the carcinogenic PAHs from the rubber.

Not surprisingly this has been the subject of extensive study. The research, over more than 30 years, suggests that the carcinogenic ones stay firmly put in the rubber. This is because they are too high boiling to pose vapour risks (at rubber manufacturing or service temperatures) and too insoluble in water to pose leachate risks.

15. Are PAHs encountered elsewhere?

They are widely distributed in nature as products of combustion (smoke). PAHs, including the carcinogenic ones, are common air pollutants. In the UK and elsewhere, PAH levels in air are routinely monitored as part of concerns over air quality.

vehicle exhausts
power generation
space heating
fires, etc. ⇒ PAHs in the atmosphere

The high stability of PAHs makes them persistent environmental pollutants. Intense heat is the trigger to their formation and they are encountered in a number of cooked foods.

16. What comes out by leaching?

It depends on what you leach with. An organic solvent can penetrate and swell the rubber, and thus disrupt the associations which would otherwise serve to retain species within the rubber.

With the right solvent, various of the chemicals from manufacture can be extracted from the rubber. Even PAHs can be extracted in this way. But this is only possible with a good solvent (i.e. an organic solvent) for the rubber. Water is not a good solvent for rubbers: EPDM and the tyre rubbers are especially resistant to water.

17. What about extraction by grease and sweat from skin contact?

It is possible that extended skin contact could remove species from rubber, and this might result in contact dermatitis for people who are sensitive to the species concerned.

It may not be a common effect, but this is a known condition: chemicals on the surface of the rubber are believed to be responsible. Intimate contact, typically involving pressure, is required and problems, where seen, are usually associated with elasticated clothing.

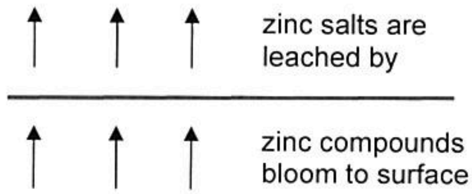
Where tyre rubber is concerned, the Danish Environmental Protection Agency has studied the usage of tyres in children's playgrounds and the likely contact scenarios. These include skin contact for up to an hour per day and possibly even some oral intake. This detailed investigation concluded that the potential health risk is insignificant.

18. Can anything be extracted with water?

Anything already on the surface of the rubber, or which can easily migrate to the surface of the rubber, is potentially available for extraction by any contacting liquid – whether or not the liquid is a good solvent for the rubber.

Rubbers have a tendency to 'bloom' certain chemicals to the surface, and those chemicals do include water-soluble species.

There is a selectivity at work here which can facilitate certain losses to water. Zinc, which is commonly used as zinc oxide, can be lost in this way.



19. Has zinc been found in leachates from rubber granulate?

Yes, but the effect is pH dependent. Acidic waters are far more effective at extracting the zinc. Zinc leachate testing already figures in a German standard for synthetic turf areas, and environmental compatibility must be included in harmonised European standards.

Whilst zinc is essential to life, the tolerance levels vary from species to species, and concerns have been expressed on the impact on aquatic species (such as the water flea) in the immediate vicinity of the granulate. The same concerns have been voiced over the environmental impact of the rubber dust generated in tyre wear.

20. What's best for the environment?

Whether or not there is a localised environmental impact (from zinc) is a matter of debate. Piles of waste tyres are a matter of fact. The UK alone produces 440,000 tonnes of waste tyres every year. Waste tyre dumps are unsightly, and present a breeding ground for disease and a target for vandals.

The waste tyre mountain cannot be ignored, and any responsible use of waste tyres has to be applauded. On this basis, rubber granulate derived from tyres offers substantial environmental benefits.